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# CONTENTS

	PAGE
CHEMICAL ENGINEERING, PLANT AND MACHINERY	
<i>By G. Edwards and F. Rumford</i> - - - - -	5
GAS, DESTRUCTIVE DISTILLATION, TAR AND TAR PRODUCTS.	
<i>By G. E. Foxwell</i> - - - - -	37
INTERMEDIATES AND COLOURING MATTERS.	
<i>By D. A. W. Adams, E. L. Johnson and J. Wardleworth</i> - -	65
IRON AND STEEL. <i>By G. E. Speight and D. J. D. Unwin</i> -	103
NON-FERROUS METALS. <i>By J. C. Chaston</i> - - - -	127
ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES.	
<i>By A. W. Hothersall</i> - - - - -	148
ACIDS, ALKALIS AND SALTS. <i>By V. W. Slater</i> - - -	164
FUEL. <i>By F. A. Williams</i> - - - - -	195
MINERAL OILS. <i>By A. E. Dunstan</i> - - - - -	216
FATS, FATTY OILS AND DETERGENTS. <i>By N. D. Sylvester</i> -	235
GLASS. <i>By R. E. Bastick</i> - - - - -	256
CERAMICS, REFRACTORIES AND CEMENTS. <i>By S. W. Ratcliffe</i> -	274
THE PROTEIN FIBRES. <i>By David Traill</i> - - - - -	295
CELLULOSE AND TEXTILE CHEMISTRY. <i>By S. M. Neale</i> - -	309
PULP AND PAPER. <i>By E. L. Hill</i> - - - - -	322
PLASTICS. <i>By Members of the Plastics Group</i> - - - -	338
RESINS, DRYING OILS, VARNISHES AND PAINTS.	
<i>By Members of the Oil and Colour Chemists' Association</i> -	377
RUBBER. <i>By S. A. Brazier</i> - - - - -	399

	PAGE
LEATHER AND GLUE. <i>By W. E. Braybrooks</i> . . . .	420
INSECTICIDES. <i>By A. B. P. Page</i> ' . . . .	435
AGRICULTURE AND HORTICULTURE—INTRODUCTION.	
<i>By A. G. Pollard</i> . . . . .	453
STARCH. <i>By J. W. Corran</i> . . . . .	492
SUGARS. <i>By M. Stacey</i> . . . . .	504
FOODS. <i>By T. N. Morris</i> . . . . .	520
THE FERMENTATION INDUSTRIES. <i>By L. R. Bishop and T. J. Ward</i>	546
MEDICINAL SUBSTANCES. <i>By N. R. Campbell</i> . . . .	573
ANTIBIOTICS. <i>By F. A. Robinson</i> . . . . .	603
ESSENTIAL OILS, ISOLATES AND DERIVATIVES. <i>By G. R. A. Short</i>	620
PHOTOGRAPHIC MATERIALS AND PROCESSES.	
<i>By H. Baines and P. C. Burton</i> . . . . .	633
SANITATION AND WATER PURIFICATION. <i>By B. A. Southgate</i> .	652
INDEX . . . . .	670

# REPORTS

ON THE

## PROGRESS OF APPLIED CHEMISTRY

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### CHEMICAL ENGINEERING, PLANT AND MACHINERY

*Chemical Engineering Group*

By G. EDWARDS, Ph.D., B.Sc., A.R.I.C., A.R.T.C., A.M.I.Chem.E.,  
and F. RUMFORD, Ph.D., B.Sc., F.R.I.C., M.I.Chem.E.

A STEADY increase in the amount of published information over the last year is reflected in the following fuller Report, but there are still some considerable delays in the appearance of complete reports of certain papers. A characteristic feature of the year has been the way in which new information was presented at conferences dealing with specific aspects of chemical technology. Meetings of particular interest to plant technologists have been devoted to "Dust in Industry," "Heat Transfer," "High Vacua," "Refrigeration Practice," and "Oxygen Production." In some of these, the papers have been made available in a special edition, a step which makes ready appraisal and comparison particularly straightforward.

#### Fluid flow

Expanding application of the gas turbine is arousing interest in the study of fluid flow at supersonic velocities. G. A. Hankins and F. W. Cope<sup>1</sup> describe some of the features of new high velocity wind tunnels at the National Physical Laboratory and discuss special techniques of measurement at high Mach numbers. The optimum conditions for efficient rocket propulsion are laid down by W. H. Wheeler.<sup>2</sup> A high ratio of fuel to motor weight is necessary and as rockets are designed for short life generally, simplification of the control valve system is advantageous from the points-of-view of both weight and reliability. Existing motors depend for efficient operation on dissipation of energy in the combustion chamber at approximately 5 million B.Th.U./cu.ft./min. Although in prolonged flight the chamber is kept cool by circulation of the liquid propellants, an obvious problem in materials of construction is introduced. Fuels suitable for rocket propulsion must burn vigorously and may give rise to unstable flame characteristics. N. P. Bailey<sup>3</sup> describes experiments under these conditions where thermocouples in the flame indicated temperatures nearly 200° c. higher than the overall flame temperature. A series of explosions occur when hydrogen-air mixtures are burned in a parallel walled tube, the periodicity being related to the resonance frequency of the tube. R. C. Binder and

A. S. Hall<sup>4</sup> have studied the effect on internal combustion engine performance of gas vibrations in the inlet manifold. The results at this stage are of limited application, but it is of interest that these workers have utilised in their analysis the analogy to electrical impedance, of the ratio of "excess pressure amplitude" of the gas to its "velocity amplitude." This utilisation of electrical similarities in the study of fluid flow and heat-transfer problems is gaining popularity. C. Concordia and G. K. Carter<sup>5</sup> have utilised a network of electrical resistors to study the flow pattern about a multi-bladed impeller. Their attention was confined to the case of an impeller with negligible end effects but the method could be developed to embrace more complex conditions.

The problem of predicting pressure drop through beds of granular material continues to receive attention. Three papers by L. E. Brownell and D. L. Katz<sup>6</sup> give detailed consideration to the problem of fluid flow through filter cakes such as are formed on a rotary vacuum filter. Introduction of additional terms in the application of Reynold's number and friction factor allow for variation due to porosity, shape and roughness of the particles of the bed. The authors then analyse the case where two fluids, only one of which "wets" the solid, flow through the cake simultaneously. In addition to the increased number of variables introduced in the flow equations by the presence of two fluids, a new factor called "effective saturation" is involved. This is defined as the ratio of voids containing only the wetting fluid to those in which both fluids are flowing. The derived equations are applied to the case of a rotary vacuum filter where washing of the cake is effected by water spray. M. Leva and M. Grummer<sup>7</sup> show that increased roughness in a particulate solid increases the voidage in dumped packing to such an extent that no increase in pressure over smooth particles is noted when a fluid flows through the bed. If steps are taken to keep voidage constant, roughness can double the pressure drop. M. Leva<sup>8</sup> draws attention to differences in available data on pressure drop in packed towers. An equation for pressure drop through packing has been devised from comparison with fluid flowing through pipes and this has proved suitable for various smooth packings, including heterogeneous material, for the range  $Re = 200-15,000$ . Pipes of 0.824 to 3.068 in. were used in the experiments. D. F. Boucher and C. E. Lapple<sup>9</sup> note a similar divergence of published data on the pressure drop in flow across tube banks. They have made a very extensive review of literature on this subject. It is clear that no single formula will account for more than a few variations in tube bank arrangements and operating conditions.

Many patents are still being issued for pumping devices. A novel form of pump particularly suited to viscous fluids is described by Lockers, Ltd., and J. R. Locker.<sup>10</sup> It consists of a chamber fitted with a flexible diaphragm which is magnetically vibrated from a 50 c/s. mains supply. The inlet port to the chamber is near the upper edge of the diaphragm and the outlet port, which is larger than the inlet, is directly opposite the face of the diaphragm. When liquid from a head tank is admitted to the inlet of the pump, the forward movement of the diaphragm forces it through the outlet port. On the return stroke more liquid flows in from the head vessel. It is claimed that with viscous liquids no valves

are required. Messrs. Barr & Stroud, Ltd., and C. D. Macgill<sup>11</sup> describe a pump consisting of a cylindrical chamber of oil-resistant rubber which is supported externally by a metal cylinder with a longitudinal opening through which a mechanically operated pressing device flexes the rubber chamber. Intake and outlet valves are also of oil-resistant rubber and the pump is suitable for handling such abrasive mixtures as oil and ground glass or carborundum suspensions. Patents have been granted to H. R. Hill<sup>12</sup> and to G. F. Jones<sup>13</sup> for pumps of variable output and to the Crane Packing Co.<sup>14</sup> for a new pump gland of the bellows seal type. The non-packed gland system using metal or rubber bellows and a spring-loaded sliding contact ring is gaining popularity because of its trouble-free efficiency. In a series of articles I. Karassik<sup>15</sup> reviews the performance characteristics of centrifugal gas compressors. The author gives many interesting and practicable tables with graphs relating to their application, and practical deviations from the theoretical constants for compressors are stressed.

Applications of "fluidised solid" technique continue to increase. R. P. Kite and E. J. Roberts<sup>16</sup> draw attention to its use in calcination of calcium carbonate, and in the combustion of pyrites, while a patent by M. H. M. Arnold and I.C.I., Ltd.<sup>17</sup> covers its use in solid-solid reactions. R. H. Wilhelm and M. Kwauk<sup>18</sup> have conducted experiments on the mechanism of fluidisation. Their experiments were conducted in three inch and six inch diameter vertical tubes using water and air as fluidising media. A wide selection of solids was considered of sizes varying from 0.3 to 5 mm., and in density from 1.1 to 10.8. From measurements of pressure drop, percentage voids and velocity they conclude that correlation can be established on the basis of four dimensionless groups. Complex friction and fluid drag factors are introduced which involve the square of the Reynold's number. The characteristics of the experimental curves obtained are similar to those previously reported by J. D. Parent, N. Yagol and C. S. Steiner.<sup>19</sup> Pressure drop increases sharply with increasing velocity until fluidisation occurs, when there is little change in pressure drop with rising *Re*. This state continues up to the velocity where rapid carry-over begins. Wilhelm and Kwauk suggest that two states of fluidisation exist, depending on whether the particles of solid have particulate or agglomerated form in the fluid state. Generally water gives rise to particulate fluidisation while gases yield aggregated fluids. Electrical charges may be responsible for the aggregated nature of fluidised solids. A study has been made of friction in the flow of of gaseous suspensions of solids by E. G. Vogt and R. R. White.<sup>20</sup> Results of vertical and horizontal flow of sand, steel shot and clover seed in a cyclic system of 0.5 in. piping are reported and a general equation correlating the results is deduced.

### Heat transfer

A symposium on heat transfer in the June, 1948, issue of *Industrial and Engineering Chemistry* indicates the general trend of advancement in this field. Stress is laid on heat transfer in packed space and in systems involving fins. W. E. Dunn and C. F. Bonilla<sup>21</sup> have derived equations for evaluating the upper and lower limits of heat transfer for

a finned system assuming (a) complete non-mixing conditions, and (b) complete mixing in fluids on the fin side. In another paper by C. F. Bonilla<sup>22</sup> shows how rearrangement of the terms in existing equations connecting local heat transfer in fins to the overall heat transfer coefficient obviates the necessity of trial and error calculations. The results are expressed in graphical form. A typical calculation shows that the use of the graph gives a value nearer than the sixth approximation by the more conventional method. An "electrical analog" has been applied by C. F. Kayan<sup>23</sup> to the fin problem. The instrument clearly shows the distortion of constant temperature lines at the base of the fin, both on the fin side and remote side of the base. Two systems have been considered, one a thin highly conducting fin and wall, and one analogous to a concrete floor attached integrally to a concrete wall with warm air "inside" and cold air on the other side. The latter model is also used for the case where the air above and below the "floor" is at different temperatures.

A comprehensive investigation of Fränkl packed heat regenerators of the type used in gas liquefaction plant is described by G. Lund and B. F. Dodge.<sup>24</sup> The effect of the dimensions of the packing,  $L/D$  ratio, reversal time and rate of flow are discussed. Attention is directed to departure from mathematically ideal conditions by the presence of water vapour in the inlet gas. By the introduction of a "thermal storage factor" good linear relationship is established between the heat transfer and Reynold's number. The film heat transfer coefficient has a slope with respect to  $Re$  higher than the Dittus Boelter equation suggests. The  $L/D$  ratio has a pronounced effect on the heat transfer coefficient and the use of a power of this ratio with the storage factor gives a general equation relating  $U$  and  $Re$ . The result is one involving a higher power of  $Re$  than usual—1.48. Correlation of results with the Fanning expression gives a friction factor which decreases non-linearly with  $Re$  although the flow should be viscous. The use of a simple separating piece between individual packings gives a higher friction factor than when the packing units are simply stacked one on top of the other. The practical design of regenerators is dealt with and numerical examples of the application of the derived equations are given. G. O. G. Löf and R. W. Hawley<sup>25</sup> describe measurements in the heating of a bed of granitic gravel. Experiments were conducted with beds of fairly closely screened particles between 0.19 and 1.5 in. diameter with air velocities from 12 to 66 cu.ft./min./sq.ft. of section. With dumped packing (*i.e.*, normal voidage) the equation which best fitted the results was  $h = 0.79(G/d)^{0.7}$ . Saunders and Ford<sup>26</sup> for heat transfer to spherical particles quoted  $h = 0.152(G/d)$  and the divergence would appear to be more than can be accounted for by the difference in shape of the particles. Furnas<sup>27</sup> had given an equation almost exactly the same as that by the present workers, except that he introduced an additional product term  $1/d^{0.2}$ . The present investigators find this term unnecessary in consideration of their experiments. Two important papers on heat transfer in packed space are by M. Leva and M. Grummer *et al.*<sup>28</sup> They advance rather more complex expressions for the heat transfer coefficient and distinguish between heating and cooling. Their experiments on cooling were carried out on a tube packed

with spheres, but in the heating experiments irregular particles were also examined and found to give the same result if the arithmetic mean diameter was used instead of the spherical diameter. Conductivity of the packing had a pronounced effect on the heat transfer but surface roughness had little effect. The inclusion of the Prandtl number was considered and rejected as being unnecessary under these conditions. It is shown both theoretically and experimentally that maximum heat transfer occurs for a packing/tube diameter ratio of 0.153.

M. S. Brinn, S. J. Friedman, F. A. Gluckert, and R. L. Pigford<sup>29</sup> show that heating a granular material (Ottawa sand and crushed Ilmenite ore,  $\text{FeTiO}_3$ ) which is flowing through a vertical tube suggests a rodlike flow with heat transfer from the hot wall to the solid as for a stationary bed. Heat transfer can then be calculated from the Graetz number (equivalent to Fourier's modulus) for unsteady-state heating of a cylinder. This means that for a given mass-rate of flow the temperature change is independent of the diameter of the tube. The heat transfer coefficient can be varied at will by altering the diameter of the tube. Experimental work was conducted using steam as the heating medium, but an extended mathematical treatment dealt with the rate of heat transfer when the temperature of the heating medium also changes, as, for example, in a contraflow heat exchanger. Another paper in the Industrial and Engineering Chemistry Symposium dealing with the application of the Graetz equation to heat transfer is by V. R. Deitz and H. E. Robinson,<sup>30</sup> and is concerned with the heating of bone char in vertical revivifying kilns. These workers also show that throughput is independent of the diameter of the retort and depends only on the initial temperature of the char and on the wall temperature.

The effect of temperature on heat transfer and mass transfer is the subject of a paper by E. W. Comings, J. T. Clapp and J. F. Taylor.<sup>31</sup> Single tubes held at right angles to a stream of air in a duct were heated electrically and by steam, and the heat transfer measured from the theoretical electrical input and steam condensate respectively. Mass transfers were evaluated by the loss of water from a similar tube coated with absorbent paper and continuously supplied from a feed weir. The degree of turbulence of the air ( $Z$ ) could be varied by baffle systems. It was found that at low Reynold numbers a 20% increase in turbulence raised the heat transfer coefficient by 25%. Change of velocity had a more pronounced effect on the heat transfer rate than degree of turbulence. Another paper of the symposium describes the work of C. C. Winding and A. J. Cheney.<sup>32</sup> To determine local mass transfer coefficients, these workers used preformed rods of cast naphthalene, of circular, streamlined, and flat sections, supported vertically to a stream of air in a duct, and they measured the loss of naphthalene by sublimation from different parts of the periphery of the sections. Heat transfer rates were deduced from the mass transfer results by the use of Chilton and Colburn's analogy.<sup>33</sup> The method is simple and should be capable of wide application.

J. Heuler<sup>34</sup> shows that even at 2000° F. convective heat transfer still represents a large fraction of total heat transfer and recommends the utilisation of this in special furnaces for rapid heating of steel. On the

other hand, M. J. Sinnott and C. H. Siebert,<sup>35</sup> from experiments in heating steel plates in a recirculating furnace, with air as the working fluid, show that a sharp drop in the convective heat coefficient takes place at 1000° F.

Only two papers on heat transfer under conditions of boiling and condensation are recorded in the symposium. C. F. Bonilla and A. A. Eisenberg<sup>36</sup> give results for heat transfer to boiling water-styrene and water-butadiene mixtures. Considerable superheating appears to occur and higher temperature differences must be maintained in boilers to effect the same boiling rate as with the pure liquids. Interfacial tension between the liquids might account for this but no information is available. D. A. Edwards, C. F. Bonilla, and M. T. Chichelli<sup>37</sup> find that in the condensation of water, styrene, butadiene, water-styrene and water-butadiene, heat transfer coefficients much higher than those predicted by theoretical consideration are obtained. Water is 6%, butadiene 40%, and styrene 129% higher than indicated by the Nusselt equation and styrene-water and butadiene-water mixtures were 43 and 34% higher respectively. Comparison with other equations for film transfer coefficients showed that the Nusselt expression most nearly agreed with the experimental results and at least erred on the conservative side with regard to condenser area calculations. The use of finned tubes for boiling and condensing surfaces is gaining popularity in refrigerating plant. Papers by D. L. Katz *et al.*<sup>38,39</sup> describe experiments on the condensation of fréon, propane, butane, sulphur dioxide and methyl chloride on finned tubes and show that a modified Nusselt equation may be used to evaluate the heat transfer coefficient. An "efficiency factor" for fins, based on their dimensions, is used to account for the additional temperature drop along the fin. Finned tubes give more than twice the condensate obtained from plain tubes of the same diameter. W. E. Ziemann and D. L. Katz<sup>40</sup> show that finned tubes of four times the superficial area of plain tubes give twice the total heat transfer in boiling isobutane and *n*-hexane.

More fundamental data on boiling are given by W. H. McAdams, J. N. Addoms, P. M. Rinaldo, and R. S. Day<sup>41</sup> who studied heat transfer from single platinum wires to water. Heat flow increases rapidly with temperature difference from 4 to 10° F., when nuclear boiling begins and the rate of heat transfer increases still more rapidly up to 47° F. Here film boiling commences and the heat transfer falls with increasing temperature difference. Between 1350 and 2550° F. a further increase in heat transfer occurs. Exploratory tests on the effect of pressure suggest that very high values of heat flux— $2 \times 10^6$  B. Th.U./sq.ft./hr.—can be obtained at pressures of the order of 1200 lbs./sq.in. without breakdown of nuclear boiling. These results are confirmed in independent experiments by E. A. Farber and R. L. Scorah<sup>42</sup> who, in addition, find that the maximum rate of heat transfer in nucleate boiling occurs at different temperature differences depending on the metal surface used. The foam-inhibitive effect of polyamides in boiling water is the subject of papers by A. L. Jacoby and L. C. Bishmann<sup>43</sup> and L. O. Gunderson and W. L. Denman.<sup>44</sup> The mechanism of action of the polyamides is speculated upon, but little direct experimental evidence of the various theories is presented. There seems little doubt that polyamides associated

with a vapour bubble will have a striking effect on the vapour-liquid interface because of their polar properties, but experimental evidence of the effect appears to be limited to direct observation of the size of bubbles generated on a heated surface.

The use of oxygen enriched air in industrial high temperature furnaces has made necessary fundamental research on fuel combustion. H. R. Fehling<sup>46</sup> discusses various aspects of the problem and gives comprehensive heat content-temperature diagrams for combustion of solid, liquid and gaseous fuels in oxygen enriched air. Dissociation of gases at the temperatures involved is appreciable. G. Ribaud<sup>46</sup> describes experimental measurements of the emissivity of carbon dioxide and water vapour in flames, and that of  $0.3 \mu$  carbon particles produced by the cracking of hydrocarbons in the combustion. Addition of heavy oils and tar to town gas increased an emission factor from 0.15 to 0.4. It is pointed out that increases of emissivity to a much greater extent would lead to serious overheating in furnace arches and would nullify any advantages in heating value. A novel application of the regenerative furnace principle is dealt with by N. Gilbert and F. Daniels.<sup>47</sup> In a furnace using two similar chambers, packed with magnesia pebbles, as furnace and regenerator, temperatures as high as  $2100^{\circ}\text{C}$ . have been attained. At this temperature oxygen and nitrogen combine to form 1.7%  $\text{NO}_2$  and this is chilled so rapidly in the regenerating chamber that 1.0%  $\text{NO}_2$  can be recovered. Development is continuing and the system might be the basis of an industrial nitrogen fixation process. A regenerative furnace process of a similar type in which methane is converted to acetylene in passage through a bed of carborundum, which on the reverse cycle is heated by gas combustion, is the subject of a patent.<sup>48</sup>

In view of the widespread interest exhibited in the first publication of the Norwich Heat Pump there have been remarkably few papers of experiments on similar devices. J. A. Sumner<sup>49</sup> describes the Norwich heat pump which uses sulphur dioxide as a refrigerant. Heat is abstracted in the evaporator section by river water and the condenser water is used for space heating. A performance coefficient of 3.45 is obtained and, even after account is taken of all mechanical expenditure on auxiliary equipment, the annual cost of operation is still less than that for operating coal fired boilers. The use of the heat pump with air both as working medium and heat source is recommended by T. F. Thomas<sup>50</sup> where space heating requires a large number of air changes per hour. No comparison is made here with coal firing but the cost of operation is very much less than for electrical heating. S. W. Andrews<sup>51</sup> shows that the efficiency of production of electrical power in this country, and particularly that produced with coal as the source of energy, leads to high electrical costs and he suggests that no advantage can be obtained from the heat pump. K. W. Miller and M. C. Penfold<sup>52</sup> show that the cost of operating a heat pump is reduced by the use of an internal combustion engine in place of an electrical drive.

### Mass transfer

The use of extractive and adsorptive processes for mass transfer is still expanding. Furfural is becoming more widely available and this

adaptable solvent is being applied in America to many extraction processes. Immiscibility with aliphatic oils and remarkable affinity for unsaturated hydrocarbons makes it ideal for drying oil purification. S. W. Gloyer<sup>53</sup> describes laboratory and large scale apparatus for the treatment of low grade linseed oil to yield an oil of high drying qualities. Similarly, extraction of soya oil gives a product of equivalent drying properties to linseed oil. The low energy requirements of the liquid-liquid extraction process make it particularly attractive from the industrial point-of-view. L. C. Kemp, G. B. Hamilton, and H. H. Gross<sup>54</sup> give a long list of improvements in viscosity of lubricating oils and of a certain number of fuel oils produced by furfural extraction. R. L. Kenyon, S. Gloyer, and C. C. Georgian<sup>55</sup> describe a solvent extraction plant for treatment of vegetable oils with furfural. 500-2000 Gallons of oil can be processed per day in the semi-commercial plant described. Full details are given of the packing of the solvent columns, the rates of throughput, reflux ratio and solvent/oil ratio. A novel feature of the plant is the use of a second liquid-liquid extraction stage where the high iodine value oil is extracted from the furfural with high boiling naphtha (paraffinic hydrocarbons b.p. 290-360° F.). F. Lerman, A. B. Kennedy, and J. Loshin<sup>56</sup> describe a pilot plant for counter current liquid-solid extraction with a capacity about 1 cu.ft. of solids per hour. The extractor consists of a number of connected stages each fitted with agitator paddles which serve the double purpose of moving the mass of solid forward stage by stage and exposing fresh surface to the solvent. This is an interesting type of extractor but unfortunately few experimental details are given and it is difficult to compare its efficiency with more common extraction plant. R. L. Kenyon, N. F. Kruse, and S. P. Clark<sup>57</sup> review the solvent extraction process for soya beans and compare it with the pressing system. The difficulties of extraction are closely allied with the pre-drying of the beans, which must yield a crushable but non-dusty mass. Although only 28% of the annual yield of soya bean oil in America is produced by this method it has already proved more economical than the pressing process and is expected to supersede the latter. A particularly interesting paper on liquid-solid extraction is that by H. P. Fan, J. C. Morris, and H. Wakeham.<sup>58</sup> They show that if sections of peanut kernel are selected to avoid broken and distorted cells extraction closely follows the theoretical Fick's law. No effort has yet been made to modify Fick's law to apply to the practical extraction of nut kernels. A considerable variation in thickness of sections always occurs in practical crushing or slicing and this alone renders the application of fundamental laws to liquid-solid extraction exceedingly difficult.

During the past year research into the adsorption of gases has generally been of a fundamental nature. E. Wicke<sup>59</sup> has examined the effect of a displacing gas on the concentration of a second gas at the end of the displacement period. It is shown that in a separation of propylene and propane on ignited bauxite, the propane cut is rendered more complete than would be expected from its adsorption isotherm by the presence of the propane. E. Wicke and U. Voigt<sup>60</sup> show that three mechanisms account for the rate of diffusion of a gas through porous surfaces. These are normal gaseous diffusion through large pores, molecular flow in pores

of diameter less than the mean free path of the gas, and surface diffusion by migration along the walls of the pores. These effects vary differently with temperature and pressure and may thus be distinguished. With carbon dioxide and nitrogen mixtures Wicke and Voigt prove that for sintered glass ordinary gaseous diffusion predominates, though at low pressures the mean free path can be sufficiently great to give evidence of molecular flow. The first two types of diffusion are always detectable in active charcoal and there is some evidence of migratory diffusion. In catalysts which operate by adsorption these effects must be considered. In high pressure synthesis gaseous diffusion is reduced and a high rate of reaction is dependent on the catalyst exhibiting high molecular and surface diffusion. The existence of surface diffusion in a compressed and reduced nickel catalyst is clearly shown in experiments with hydrogen and hydrocarbon gases at low pressures (3 mm.) and it can be shown that poisoning the nickel surface reduces the migration of gas molecules along the surface with a corresponding reduction in catalytic activity. A. E. Hirschler and S. Amon,<sup>61</sup> in a study of adsorption of hydrocarbons on silica gel, show that in the case of sigmoidal isotherms the substance in low concentration is preferentially adsorbed. Mixtures of *n*-heptane and methyl-cyclohexane show this effect and either compound can be freed of traces of the other with silica gel. A patent<sup>62</sup> for the removal of specific constituents of a gas mixture by adsorption at intermediate stages in the compression of the gas, claims that, by utilising the power and refrigerating value available in expanding the gas residue, the process is made inexpensive. G. C. Williams, R. R. Akel and C. P. Talbott<sup>63</sup> recommend the use of fibreglass packing in liquid absorption of a gas at high velocity, where high volume efficiency is not essential.

M. J. Bogart and A. S. Brunjes<sup>64</sup> describe a new method of recovery of phenol from weak aqueous solutions involving an extractive distillation followed by azeotropic removal of residual water. The weak phenolic solution resulting from synthetic manufacture of phenol by benzene chlorination contains 17% of sodium chloride. Measurement of vapour-liquid equilibria of aqueous solutions of phenol and salt at 1 and 4 atmospheres pressure have shown that separation is improved by the presence of the salt, particularly at the higher pressure. A plant has now been constructed and operated on the following lines; the weak phenol-salt solution is fed to the top plate of a 35 plate bubble cap column operating at 4 atmospheres pressure, and from the base of this column 17% salt solution containing less than 0.01% by weight of phenol is removed and used as feed for electrolytic cells. (It is important that the brine for electrolytic cells should be essentially free from phenol.) The overhead vapours from the brine stripper condense to yield an aqueous layer (reflux) and a lower layer of 70-80% phenol. This is dehydrated under slight vacuum in a 30 plate column using toluene or monochlorobenzene to remove the water azeotropically as overhead product. Pure phenol is drawn as residue from the column.

#### *Azeotropic distillation*

The industrial use of azeotropic distillation expands almost daily, while generalisation of azeotropic effects is being attempted by laboratory

workers. A particularly straightforward approach to the behaviour of azeotropic mixtures with variation of temperature and pressure is that by W. Licht and C. G. Denzler.<sup>65</sup> These workers claim that an azeotrope should behave as a pure substance and yield straight line graphs of logarithm of vapour pressure against the reciprocal of the absolute temperature. This they show to be true in a number of cases. A new value of  $L$ , the molal latent heat of evaporation, can then be ascribed to the azeotrope. It is surprising that this new value is unaffected by pressure and temperature variation, which in many cases alter the fractional composition of the azeotrope. The problem of azeotrope composition is not considered by these workers but H. P. Meissner and S. H. Greenfield<sup>66</sup> have studied the relation between boiling point and composition of binary azeotropes. They suggest an empirical relationship but deviations are considerable. H. Skolnik<sup>67</sup> has conducted a similar investigation, but confines his theory to compounds in homologous series and obtains more consistent results. He derives a simple relationship between boiling point and percentage of entraining agent, and for boiling point of the azeotropic mixture and that of the pure entrainer. In an exhaustive investigation E. L. Piret and M. W. Hall<sup>68</sup> have attempted to clarify the confused results obtained in distilling formaldehyde solutions. Previous workers have indicated the presence of azeotropes of formaldehyde and water, but there is wide discrepancy in the proposed concentrations of the constituents. The present investigators show that partial condensation of the vapour in equilibrium stills can account for these discrepancies. The results do not yet appear to be conclusive. The separation of formaldehyde and water might be easily effected by liquid extraction. H. G. Johnson and E. L. Piret<sup>69</sup> show that formaldehyde can be extracted from water with organic solvents. Aliphatic alcohols are most suitable and addition of inorganic salts to the aqueous phase greatly enhances the partition coefficient, while temperature has little effect.

Attempts have been made to devise overall correlation of data for normal distillation, particularly with reference to petroleum products. S. T. Hadden<sup>70</sup> has shown, from a review of the extensive fundamental work of Sage and Lacey and others, that the logarithm of the vapour-liquid equilibrium constant is linearly related to the reciprocal of the absolute temperature. This might have been expected from the close dependence of equilibrium constant on relative vapour pressure but the author has extended the scope of the relation by producing nomograms with  $K$  and  $T$  as the major reference scales, correlating equilibrium data for paraffins and olefines having b.ps. up to 1100° F. at pressures from 10 to 2000 lbs./sq.in. It would appear that the chief advantage of the system over that of E. G. Scheibel and F. J. Jenny<sup>71</sup> is the fact that by suitable choice of scales all the nomogram network lines are straight and from only a few estimations it should be possible to insert readily the line representing a new compound. A. J. V. Underwood<sup>72</sup> draws attention to the errors which can occur in the "key component" solution of multi-component distillation problems and proposes a solution which allows of determination of all components at any point in a fractionating column, by introducing arbitrary relative volatilities, based on the true volatilities and reflux ratio.

A practical method of determining vapourisation data for complex mixtures is recommended by W. D. Harbert.<sup>73</sup> A boiling point curve and compositions of overhead vapour can be obtained by slow distillation of an unknown mixture in a batch fractionating column operating at high reflux ratio, and these results can be used to design a continuous column. E. Kirschbaum<sup>74</sup> has examined the loss in efficiency resulting from channelling in fractionating columns. In columns packed with Raschig rings to depths of between 25 and 400 cms. channelling results in a sharp fall in efficiency after packing height exceeded about one metre. The efficiency also depends markedly on the vapour velocity, a maximum being observed at 1.1 metre/second for columns with at least one metre of packing. An attempt has been made by C. Berg and A. C. McKinnis<sup>75</sup> to relate activity coefficients and temperature by utilising the Duhring modification of the more direct vapour pressure-temperature plot. With ethane-acetylene mixtures a straight line is in fact obtained but a graph of ethanol-water is not linear over any extended range of temperature. E. G. Scheibel and C. F. Montross<sup>76</sup> have devised a useful practical equation for determining for various reflux ratios the concentration of light and heavy key components on the feed tray of a bubble-cap column. This provides a simple method of locating the feed tray in multi-component distillation.

An interesting type of still for refining natural gum turpentine (the Reed still) is described by W. H. Shearon, E. L. Patton and G. P. Shingler.<sup>77</sup> Formerly, the purification of gum turpentine has been carried out in open fired stills or by batch steam distillation. The product of such stills was naturally of variable quality and the Reed continuous still was designed to eliminate this defect. Raw gum is heated by steam and continuously passed to a flash chamber where a preliminary separation of the rosin and turpentine takes place. The lower end of the flash chamber is integral with a wetted wall column and the rosin flows down this to a simple reboiler fitted with both open and closed steam pipes, which supply additional heat to remove the final traces of turpentine from the gum. A uniform high grade rosin is run off from this and the turpentine in the condensed vapours from the flash chamber is of particularly low acidity.

### High vacuum technology

The first high vacuum conference in this country since 1938 was held at Gleneagles; several well known American technologists were present. The proceedings are reported in a supplement to *Chemistry and Industry*.<sup>78</sup> In the opening paper S. Dushman rapidly summed up early development and went on to discuss more modern aspects. He developed a particularly simple expression for speed of pumping in the micron range based on Langmuir's classical equation for diffusion through an aperture. In a similar manner Dushman showed that the conductance of a pipe line for air at low pressure can be practically expressed as  $F = 97.75a^3/l$  litres per second when the ratio of length ( $l$ ) to radius ( $a$ ) is greater than 100. This value inserted in an equation of summed resistances gives the overall rate of evacuation in a practicable form. The difficulties of pressure measurement in the range below 1 micron were stressed. The mass

spectrometer is still the most sensitive instrument for detecting small leaks; an instrument located at any point in a vacuum unit will detect with exceptional sensitivity the presence of helium or hydrogen from a "probing jet" with which the operator scans the various parts of the system. A novel instrument suitable for detecting macro leaks has been devised by W. C. White and J. S. Hickey.<sup>79</sup> It is based on the principle that the positive ion emission from heated platinum is greatly increased by minute quantities of halogen vapour. The instrument is an open ended diode valve with a heated platinum cylinder, electrically positive with respect to a surrounding nickel ring. The apparatus under test is maintained at a pressure greater than that of the atmosphere and a quantity of carbon tetrachloride or other halogen compound introduced. Local escapes may be detected with the "thermionic halogen vapour detector."

J. C. Swallow and J. S. Gourlay described the application of high vacua in the paints and plastics industries. High vacuum has already been applied to the removal of low polymers from certain plastics and has proved successful in producing more homogeneous materials. This may have wide application in the manufacture of plasticisers where the presence of low polymers has a detrimental effect on the product. Metallisation of plastics is being carried out on a commercial scale, as illustrated by a plant by Metropolitan Vickers Ltd. for coating  $8 \times 4$  foot sheets of plastic. The metallising chamber of this plant has a total volume of 232 cu.ft. Eight condensation pumps 8 in. in diameter are used in the pumping set; and a continuous stripping system is used to remove water from the pump oil. The ultimate pressure is  $2 \times 10^{-5}$  mm. E. W. M. Fawcett, in a paper on the application of high vacuum distillation to the processing of triglyceride oils, stressed the limitations of the process. The problem of separating valuable triglycerides is complicated by the fact that the desirable compounds are often chemically combined with less useful fractions. Even for free compounds high fractionating efficiency is necessary to separate the constituents. Conventional high vacuum stills have in general an efficiency represented by something less than one theoretical plate in normal distillation and therefore offer only the advantage of lowering the boiling point.

R. S. Morse dealt with American plant development during the past war. He traced the growth of freeze drying processes leading to the modern units using scraper condensers and liquid desiccants. In the first of these, water removed at pressures down to 10 microns is collected as ice on the wall of an inclined wide tube condenser situated between the dehydrating chamber and the pumps. This ice is continuously removed by a mechanically rotated cutter and drops into a refrigerated chamber, from which it is removed at intervals. This was the process used throughout the war for drying penicillin. Pilot and large scale plant for drying orange juice was described, but this will be referred to in more detail in the later section on drying. In the liquid desiccant process the water leaving the drying chamber is absorbed in a strong solution of a salt such as lithium chloride. The diluted solution is continuously stripped of its water in an external reboiler and after cooling is recirculated to the water absorption section (cf. W. H. Tucker and

T. K. Sherwood,<sup>80</sup> who consider the specific advantages of an isothermal (wetted wall) type of absorber, and of spray absorption which follows an adiabatic law). A graph of cost of drying against working pressure exhibited by Morse showed a fairly linear increase from 0.5 cents/lb. of water removed at 300 mm. to 100 cents/lb. at 0.03 mm. The optimum operating pressure of a vacuum drying unit should therefore be the highest compatible with thermal instability of the product. Although the spinning bowl still of Hickman has undoubted advantages in low contact times, the falling film still is the most adaptable to very large scale operation. Morse stressed the fact that such stills can give large rates of throughput. In evaporating di-2-ethylhexyl phthalate rates as high as 60 lbs./hr./sq.ft. evaporating surface had been achieved, and single units with an output of one ton an hour are projected in America.

R. A. Stauffer dealt with the metallurgical aspect of high vacuum technology. The closing down of plant for vacuum production of magnesium (Pidgeon process) was due to the fact that the plant was badly situated geographically. During the war one hundred million pounds of magnesium was produced by this process, which involves the reduction of calcined dolomite with  $\text{FeSi}_3$ , or Al, at pressures of the order of 0.5 mm. The magnesium formed distils from the reaction zone and permits reduction to go to virtual completion. The same process was applied to making calcium, and plants producing magnesium by the Pidgeon process were partially converted to calcium manufacture. Modifications of the system are now being applied to the production of lithium, barium and columbium. Vacuum refining can be applied during casting operations and removes not only dissolved gases but volatile metallic impurities. It has been shown that much of the purification occurs during the pouring period rather than in the melting stage and this would suggest that the use of thinner films of metal than exist in a crucible, or the incorporation of some form of agitator, would improve the process. The vacuum process for the continuous coating of paper has been developed to such an extent that it is now competing favourably with the established methods of foil manufacture. The process was used at the Bosch factory in Germany during the war to deposit zinc on oil-impregnated paper, which was then used to produce radio condensers less bulky than the paper and foil type. In America the method has been extended to aluminium coating of cellophane for decorative purposes and coating speeds of 500 ft./min. are claimed.

The conference concluded with a paper by C. R. Burch which is not recorded in the supplement. Dr. Burch reviewed the events which aroused his original interest in high vacua and described the experiments on distillation which resulted in the well known Apiezon high vacuum products. He reviewed the general development of high vacuum technology and illustrated with numerous photographs the contributions which have been made in Great Britain. It is to be regretted that this paper was not recorded and that the photographs, many of historic importance, could not be included in the records.

Papers presented at an American conference on high vacuum include one by C. E. Normand,<sup>81</sup> who elucidates the variations which occur in gaseous flow in pipes as the pressure is reduced. A careful

mathematical analysis is presented and summed up by a rough rule that for  $pD$  (pressure in microns multiplied by diameter of conduit in inches) less than 7, Knudsen's equation for molecular flow holds. For  $pD$  greater than 220, Poisseuille's law of viscous flow applies. Between these two values the rate of flow is greater than either molecular or viscous flow rates. B. B. Dayton<sup>82</sup> reviews the various methods at present in use for measuring pumping speeds and shows that errors arise by beams of molecules from a controlled leak impinging on either the gauges or the pump throat.

On the industrial scale steam jet ejectors are being more widely applied. Five and six stage ejectors are capable of developing ultimate pressures of the order of one micron and are suitable for backing oil condensation pumps. A useful survey by H. M. Sullivan<sup>83</sup> deals with all types of pump, including a booster for use between condensation and mechanical pumps in which a single jet of oil vapour acts either on the condensation principle or as a jet ejector depending on the prevailing pressure. This paper gives measurements of the loss of efficiency which takes place when the heater rating of condensation pumps is exceeded.

The efficiency of condensation pumps in handling hydrogen is a subject of controversy. R. J. Gibson<sup>84</sup> finds that hydrogen can be pumped at one third of the speed of air in a four-inch self-fractionating pump operating on silicone D.C. 702. D. Fluke<sup>85</sup> reports that hydrogen is pumped three times as fast as air in small two-stage mercury condensation pumps while B. B. Setlow<sup>86</sup> concludes from experiments with a three-stage pump using Amoil-S that hydrogen is removed at the same speed as air but requires lower backing pressures. Gibson suggests that the vapour stream is not sufficiently dense to prevent back streaming of hydrogen. According to Setlow the speed of pumping depends on two functions, the rate of diffusion through the aperture to the jet and the rate of removal of gas by a collision process in the vapour. This might account for Fluke's observation that the speeds of pumping hydrogen, helium, air, argon and freon are in proportion to their rates of diffusion. It is clear that further research will be necessary to elucidate this effect. Setlow concludes that the jets and gaps in oil condensation pumps must be designed for specific gases if full use is to be made of the rate of diffusion at the aperture.

### Filtration and gas cleaning

Main developments this year are in the field of gas cleaning and particularly in dust removal. A special Conference held at Leeds, under the auspices of the Society of Chemical Industry, considered 23 papers on various aspects of the subject, some of which were of special interest from a chemical plant standpoint. J. H. Hellyer and J. C. Cleaves,<sup>87</sup> after a short survey of dust-collecting methods, describe modern electrostatic precipitators in some detail. Charged electrodes are now made of square-section wire twisted into screw form for maximum discharge. Earthed receiving electrodes are of steel plate for screen and wall forms, or of hexagonal section piping for the more common tube precipitators. This form of tube, in sizes up to 10 in. diameter, economises in working space while providing a large discharge area. A heavy corona discharge

ionises the dust particles, voltage requirements dropping steadily with gas density until a minimum is reached with pressures of about 76 mm. Discharge from the negative electrode is inversely proportional to cross-section, but a square of  $5/32$  in. is probably the minimum for practical purposes. The whole electrode surface must be kept as clear as possible of precipitate, and a number of rapping devices are used. Fortunately the bulk of industrial dusts remain coagulated as they fall, and do not re-disperse into the gas. Thick coatings of non-conducting dust are particularly undesirable, as they may set up a "back-ionisation" stream. Normal dust removal will give a 95% efficiency, without discrimination between particle sizes, for a pressure drop of about 1 in. of W.G. Dust-free air can be obtained from a "Precipitron" of 1 in. diameter tubes with fine discharge electrodes, followed by collector louvres with alternate charged and earthed plates. Ozone formation can be checked by using positively charged plates.

It is generally accepted that electrostatic deposition is the most certain method for dust removal, but the capital cost may be very high, especially for small installations. G. L. Fairs and E. Godfrey<sup>88</sup> have proposed a number of alternatives. Thus, while the electrostatic plant is essential in "contact" plants burning pyrites, a plant using sulphur as raw material can operate quite smoothly with a hot gas filter formed from a wall of granite chips between louvres. Dust from screening operations can be sucked away by a fan and removed from the air by a coke-packed scrubbing-box with water sprays. Even a cyclone can remove a large amount of fine dust if provided with rings of water sprays. Air may be filtered almost free from dust by aspiration through compressed slabs of slag wool—Stillite. These slabs can be built into a closed tent shape, and the filtered air drawn from the interior. Rates of 7–9 cu.ft./min. could be obtained with a pressure drop of 1 milliat., rising to 4 milliat. after 6 months, when the slabs of Stillite were discarded. This filtered air was required in rooms where transparent plastic sheets were being finished, or organic medicinals free from bacterial infection were being prepared. R. G. Carnall<sup>89</sup> dealt with a similar problem in the finishing of photographic film, and advocated the use of bag filters, with somewhat similar pressure drop and rates. The bags had a working life of ten weeks between washings, and usually were discarded after three working periods.

L. Marsden, G. W. Robertson, and R. A. Storey<sup>90</sup> deal with the elimination of dust when handling finely-divided chemicals. Casks and drums should be filled under a suction hood, while fine powders are best fed to a reaction vessel through a retractable spout with some form of vibrating device. With some filling operations it may be necessary to arrange for special sealing pads as well as these spout devices. Combustible dust presents a hazard at all times, and especially when local high concentrations may exist momentarily, as in the intermittent tapping of electrodes. The plant in such circumstances should be provided with some kind of explosion relief door. D. Matheson<sup>91</sup> proposes that the general recommendations of the Safety in Mines Research Board should be followed, and 5–10 sq.ft. of vent area per 100 cu.ft. of plant volume should be provided; this would take the form of a light metal swing door, closing down into a felt packing after opening. Fire dangers following

on, or connected with dust cloud ignition are discussed by G. V. Thom and G. A. V. West,<sup>92</sup> and they have made a list of the principal laws and regulations governing precautions to be taken, means of escape, and permissible ranges of "fire loading." J. E. Garside<sup>93</sup> describes a method for the determination of explosive limits, while E. G. Cox and A. G. Pearce<sup>94</sup> show under what conditions ignition can occur. A number of chemical and physical processes can generate electrical charges of sufficient magnitude to give an occasional spark, one of the most obvious being the flow of a dry powder down a chute. E. Jones and A. G. White<sup>95</sup> compare the characteristics of dust and gas explosions.

Published matter on dust explosions not read at the Conference includes a paper by S. H. Wilkes,<sup>96</sup> who considers that any combustible dust, in concentrations of the order of 0.02 ounces/cu.ft., in contact with a local hot spot of 600° C. or over, is likely to give rise to a dust explosion. One of the characteristics of these is that old accumulations of dust are disturbed by the explosion wave, which thus becomes self-propagating. Scrupulous cleaning of rafters and other corners of the plant is therefore an essential precaution. A review by I. Hartmann<sup>97</sup> of the factors contributing towards explosive violence and initiation shows that some dusts, such as magnesium metal powder, can ignite in a carbon dioxide atmosphere.

Methods of estimation of dust vary widely. W. B. Lawrie<sup>98</sup> describes a combination of thermal precipitation and photographic recording for the inert dusts of the iron and steel industry, while W. M. Cumming, F. Rumford and W. G. Wright<sup>99</sup> absorb a reactive dust in a chemical solution, and compare the colour produced with standards, using a tintometer. These workers also gave a method for the determination of potential dust producing qualities of solid samples. This potential dust cloud formation may also be indicated by the available surface of a sample, and P. J. Rigden<sup>100</sup> has evolved a micro technique for measuring this surface, based on permeability to gas flow.

R. W. Porter<sup>101</sup> claims that many dust clouds may be caused to agglomerate by the use of ultra sonic sound waves. An air siren driven at very high speeds by a turbine generates the intensive wave system required, and a dust with a particle size around 1 micron forms coagulated masses of 100 microns or more in size. These settle rapidly under the influence of gravity, or can be stripped out by a cyclone or similar device. The process has proved to be successful in the collection of carbon black.

## Evaporation

The design of multiple effect evaporator plant has usually been based on a series of trial and error balances, with assumed temperature differences. H. S. Ray and F. L. Carnahan<sup>102</sup> suggested some three years ago that the process could be simplified by assuming a fixed ratio between the minor heat changes, such as flash evaporation, and the major change of condensation or evaporation. J. A. Storrow<sup>103</sup> has simplified and re-stated this ratio method, and shows that results close to those obtained by the "classic" trial balance process can be obtained. The mathematical methods seem simpler and more certain than those of the older method. J. C. MacDonald and T. Rogers<sup>104</sup> have made a detailed survey of the

factors governing the concentration of a beet sugar liquor, and have presented equations for the amount of steam and the area of heating surface required for a given degree of concentration. C. B. B. Connell<sup>106</sup> considers that the capacity of a multiple effect evaporator is normally controlled by the evaporative capacity of the later, cooler effects. To overcome this limitation, he proposes to use more steam in the first two effects of a quadruple unit, and to apply surplus vapour to other purposes. This suggests immediately thermal compression to diminish primary steam usage, but whether a sufficient temperature drop for many industrial liquors could be obtained is doubtful. W. M. Stahel<sup>106</sup> has described the effective use of vapour recompression in a Swiss beet sugar works, but the compression was mechanical, and may involve very high electric power charges in this country.

Vapour recompression principles are now being applied in the construction of small evaporators for the production of distilled water. S. G. Greenhalgh<sup>107</sup> has given some account of the factors involved in design, quoting a number of figures from German practice, while G. C. Downie<sup>108</sup> has described a small portable unit. When thermally sensitive substances are being distilled under high vacuum, recourse is made to a rotating disc heating surface; this principle has now been applied<sup>109</sup> in evaporation, and is claimed to reduce contact with heating surfaces to a few seconds.

A paper from the U.S.S.R., by V. A. Rachko,<sup>110</sup> makes some novel statements on heat transfer in evaporator tubes. Heat transfer coefficients are determined only by the "heat flux" (in effect the temperature difference) and are unaltered by injection of steam at the bottom of the tube to increase circulation rates, or by the ratio of tube length to diameter. Reynolds and Prandtl numbers for the liquid side have little significance. These statements are not in accordance with the results of other workers, but show that no generally accepted rules for evaporator heat transfer can yet be laid down.

### *Mixing*

An analysis of the design of mixing vessels by E. S. Bissell<sup>111</sup> *et al.* has stressed the following features. All sharp corners should be avoided, rectangular tanks being generally undesirable, but centrally placed mixing devices should always be fitted with baffles. These baffles can take various forms, according to the work required. Thus stator rings adjacent to the central rotor give intense agitation over a small zone, and are suited to emulsion manufacture. Radial side strips give more general mixing, and should always be combined with coils for heating or cooling. The effect of such strips on power consumption has been measured by D. E. Mack and A. E. Kroll,<sup>112</sup> and they have shown that the power increases with the number of baffle strips up to a maximum of between four and six. Further increases make no difference to the power. A general formula for the power requirements under the fully baffled conditions shows that these are proportional to  $N^3 L^5$ , where  $N$  is the speed of an impellor of dimension  $L$ . The need for baffles in centrally stirred tanks is also stressed by E. J. Lyons.<sup>113</sup> He has concluded from a study of mixing patterns, that a turbine with stator ring is probably

the best form of agitator for mobile liquids, while a truncated cone is preferable for solid-liquid suspensions. A spinning disc can be used for the manufacture of emulsions, but for the dispersion of gases in a liquid, a turbine with top baffle is recommended. Paddle stirrers should be reserved for very viscous liquids, and propellor stirrers for liquids with the mobility of water or less. The ratio of mixer diameter to tank diameter should increase as the viscosity and density of the fluid being handled increases. R. B. Olney and G. J. Carlson<sup>114</sup> have measured the power involved in mixing, using some new forms of turbine mixers; they have correlated their results with those of several previous workers, and produced a nomogram for the determination of power requirements. E. S. Bissell<sup>115</sup> has laid down some practical rules for the choice of agitators, and added some details on the construction of stuffing-boxes and glands.

It has been shown to be possible to dispense with mechanical agitation altogether in the difficult problem of mixing phosphate rock and sulphuric acid. G. L. Bridger, R. A. Wilson, and R. B. Burt<sup>116</sup> describe a jet mixer with four tangential jets of acid entering the top of an inverted cone, into the centre of which the rock is fed, with the mixed stream leaving as a viscous fluid at the bottom. The cone is only 27 in. in height and 18 in. in diameter at the top, tapering to a 3 in. discharge, but can give 35 tons per hour of finished superphosphate mix. Dimensions of the cone appear to be somewhat critical, and the rock stream must enter at the centre of the vortex caused by the tangential flow of acid.

### *Drying*

The process of freeze drying is now being applied experimentally to a large number of food products, according to E. W. Florsdorf.<sup>117</sup> Costs are higher than for normal drying processes, but the improved quality of the final product may justify this extra charge. For very delicate organic materials such as penicillin or streptomycin freeze drying may be the only means of preserving the original molecule. For food products, however, the only case in which the process appears to have passed out of the experimental into the industrial field is in orange juice drying. H. W. Schwarz and F. E. Penn<sup>118</sup> have described a large plant for this operation. The juice is pre-concentrated to 50% solids in a conventional film evaporator, and then sprayed on to the walls of the vacuum drying chamber. These walls are warmed to 100° F. by water circulation, and the pressure in the chamber is maintained at 300 microns. The only ice formation takes place in the condenser, which is a rotating cylinder maintained at -40° F. Flakes of ice, condensing at a pressure of 250 microns, are scraped off into a receiver, while the dried juice is similarly scraped from the walls of the dryer. As the orange juice never appears to freeze, it is perhaps undesirable to call this process freeze drying. In a process in which the material being dried actually freezes, Florsdorf (loc. cit.) considers that ice is evaporated up to about 90% of the original water content, and then the process becomes one of moisture removal from a solid. C. J. Bradish, C. M. Brain, and A. S. McFarlane<sup>119</sup> have also noted a constant drying rate period in which a plane of separation between upper, partly dried solid, and lower, frozen layer is receding from the upper surface. When this separating plane reaches the bottom

of the solid mass, there is a sharp fall in the rate of drying. Presumably the input of heat during this process has been sufficient to keep the temperature of the solid approximately constant, while the solid phase consists of ice crystals and inert solid. It is not improbable that very soluble materials would give very different drying conditions. When, as is often the case in medicinal preparations, the substance being freeze-dried is held in a number of small containers, the problem of heating these to provide heat for evaporation can be solved<sup>120</sup> by wrapping them in a metal strip heated by an electrical current.

The distribution of natural gas over long distances makes it necessary to dry the gas extensively to eliminate blockage by ice formation and corrosion. H. C. Amero, J. W. Moore, and R. G. Capell<sup>121</sup> have compared the relative merits of a number of solid absorbents, such as silica gel and activated alumina. They find that a synthetic material known as "Florite," and made up from a mixture of inorganic oxides, has a considerable capacity for water vapour combined with a low-pressure drop through the drying zone. Drying gas by cooling encounters the difficulty of ice formation on the cooling surfaces. This may be overcome by a suggestion made by T. A. Hall and G. G. Haselden,<sup>122</sup> who have described the mixing of the gas to be dried with a supply of previously dried and very cold gas. The moisture or other condensible impurities are thrown down in the form of a "snow" which can easily be filtered from the residual gas mixture. The use of gas conveyor dryers appear to be extending, and a recent patent<sup>123</sup> describes entraining throats at top and bottom of a long uniform drying section, where the drying particles move slowly upwards.

### *Size Reduction*

Conflict of evidence on the power required for grinding solids lends interest to studies which have been made on the behaviour of particles under stresses just above the elastic limit. J. S. Kochler and F. Seitz<sup>124</sup> consider that the initial strain takes the form of a displacement of one or more atoms from their place in the crystal lattice. These imperfect areas grow until their boundaries have moved throughout the solid particle, while the total amount of energy absorbed may be very small. D. H. Bangham and N. Berkowitz<sup>125</sup> trace a connection between such areas of weakness and the presence of an absorbed film of gas. This connection may be confined to coal, for which a cellular structure rather than a crystal lattice may be assumed. Primary strain, followed by gas absorption, could then take the form of slippage at the cell boundaries. R. L. Brown<sup>126</sup> thinks that the existence of microscopic cracks and fissures determines the relative ease of size reduction, and he has traced a connection between shatter tests on coal samples and the screen analysis of the coal consignment from which the samples were taken. It is doubtful if any general rule can be traced in these matters of grinding. In the simple but very important case of wheat milling, practically the whole function of the grinding is to tear open the grain, and very little force is needed to disintegrate the kernels. It is interesting to note that the differential speed rollers which have been used for such work for centuries may be replaced by high-speed disintegrators. A. N. Hibbs, J. A.

Shellenberger, and R. O. Pence<sup>127</sup> have shown that the impact breaking of such machines can be adapted for flour milling.

The distribution of particle sizes in a finely-ground powder is held by R. North<sup>128</sup> to be a characteristic of the raw material rather than determined by the type of grinding employed. He quotes results to show that three different types of air-swept mill produced the same size range when the sample was ground to a standard upper limit. It is doubtful whether open and closed circuit grinding would not show a substantial difference. The same consideration of standard size distribution is perhaps behind the proposal of R. L. Brown,<sup>129</sup> that a simplified form of screen analysis for coal should be based on the ratio between two specific sizes.

H. Heywood<sup>130</sup> urges that attempts should be made to standardise particle size analyses. At present these may be made by processes of geometrical similarity, hydrodynamic similarity, and gravimetric similarity. The three methods are compared and criticised, together with the less important methods for derivation of particle size from surface measurement. A process is proposed for the expression of size analysis in a graphical form, and reduction of this to a "mean particle size." P. E. Bugge and R. H. Kerlogue<sup>131</sup> have devised a simple procedure for the determination of surface area by adsorption isotherms with elimination of the need for "dead space" measurement.

E. N. Simons<sup>132</sup> has developed a new form of "whizzer" air classifier, with multiple discs for throwing the solid and a wide range of adjustment to the tangential air-ports. S. C. Lyons and A. L. Johnson<sup>133</sup> have published an account of the performance of a Bird continuous centrifuge working as a classifier. The plant may be easily controlled and gives a relatively dry discharge, but capital charges are high and all moving parts wear rapidly.

Normally, size reduction is a process involving solids, but the fine disintegration of a liquid stream may be considered as a branch of the process. A large amount of empirical operation is available on the operation of various types of spray, but, to the writers' knowledge, no attempt has been made to correlate spray forms with the fundamental physical properties of the spraying system. H. C. Lewis, D. G. Edwards, M. J. Goglia, R. J. Rice and L. W. Smith<sup>134</sup> have tried to develop such a relationship for the atomisation of a liquid stream in the gas stream of a Venturi throat. The work was carried out as a war-time project for the better understanding of smoke cloud formation, and an application of the process has been described by E. W. Comings, C. H. Adams, and E. D. Shippee.<sup>125</sup>

### **Boiler water treatment**

Until the appearance of synthetic ion-exchange materials, removal of scale-forming constituents from boiler water followed the century-old practice of lime-soda treatment with only minor changes, except where low solid content and negligible temporary hardness allowed the use of natural zeolites. Ion-exchange processes are developing so rapidly that it is possible that they may displace all other methods, especially for the higher pressure boiler plants in which the feed must approximate to

distilled water. F. R. Riley and H. M. Day<sup>136</sup> show how the newer types of resin agents can be made up into a plant for complete demineralising at a running cost which for most industrial waters is well below that of distillation. The initial cost of the resin may be high and the effective life has not yet been fully established. One great advantage of these plants is that they can be made fully automatic, with devices to change streams from one resin bed to another, as described by D. J. Saunders.<sup>137</sup> This plant combined demineralised water with a condensate return, while another was combined with a lime softening system. E. G. Kominek<sup>138</sup> has drawn up balance sheets of American practice to show that ion-exchange is cheaper than distillation for all waters containing less than 30 grains per gallon of ionised salts. It is possible that the higher relative cost of fuel, and hence of steam in Great Britain may raise this 30 grains/gallon limit very considerably.

S. D. Distelborst<sup>139</sup> shows that one of the principal difficulties in the application of ion-exchange methods to boiler waters is, as with the older processes, the elimination of silica. The solution he proposes is to add NaF to the raw water; this, on passage through the cation exchange material is converted to HF, which forms a complex with the silica. Instead of air blowing at this point (cf. 1947 Report) the water passes direct to the anion exchange material, where the silica is absorbed, probably as  $\text{SiF}_6$ . This method is also commended by W. C. Bauman, J. Eichhorn and L. F. Firth,<sup>140</sup> but they have proposed two alternatives. The first is to add HF directly to the water after it has passed the cation-exchanger, and the other is to mix grains of an insoluble fluoride ( $\text{CaF}_2$ ) with the resin pellets of the cation-exchange bed. The regeneration of anion-exchange resins containing  $\text{SiF}_6$  by the direct use of alkaline solutions tends to give silica deposits, but these may be avoided by a primary wash with strong salt or acid solutions. All these methods involve the handling of fluorides in some form, and this may be avoided if the anion-exchange material is sufficiently basic to absorb the silica direct from solution. According to V. J. Calise<sup>141</sup> and M. Lane, resins of this strongly basic type can be prepared from substituted amines. In similar fashion, strongly acid cation-exchangers can be built up from organic complexes containing sulphonic acid groups. W. C. Bauman, J. R. Skidmore, and R. H. Osmun<sup>142</sup> claim that such resins are stable to hot water, changes in changes in  $p_H$  and to oxidising conditions.

The use of expensive ion-exchangers to remove temporary hardness can be avoided by a combination process described by J. G. Walker.<sup>143</sup> The water is limed to remove temporary hardness and magnesium salts in the usual way, but no large settling tank is used. The water with some material in suspension flows to a "calcium-removing" resin material, which absorbs excess lime and the residual unsettled carbonates and hydroxides. The effluent can be softened by a normal base-exchange process. The first resin is regenerated at intervals by treatment with hydrochloric acid. W. L. Tanzola, R. L. Reed, and J. J. Maguire<sup>144</sup> have noted the successful use of barium carbonate for softening during a temporary shortage of soda ash. A British Specification<sup>145</sup> for boiler water treatment has appeared recently, and an article by P. Hamer<sup>146</sup> on the relative methods of softening may be of interest.

According to a recent patent,<sup>147</sup> many of the corrosion and scale-forming tendencies of softened boiler water can be overcome by increasing the ratio of potassium to sodium ions to more than 0.5. This can easily be done by substituting  $K_2CO_3$  for the sodium salt in lime soda treatment, or by the use of KCl in regeneration of base-exchange materials. L. E. Hankinson and M. D. Baker<sup>148</sup> describe a localised corrosion effect in a boiler tube, with embrittlement under a deposit of  $Fe_3O_4$  associated with small quantities of feed water impurities. They trace the corrosion to tube cleaning by acids followed by the use of water with a high oxygen content. F. G. Straub<sup>149</sup> considers direct attack on steel by free caustic alkali to be the principle cause of corrosion in high-pressure boilers, but E. H. Mitsch and B. J. Yeager<sup>150</sup> believe that air leakage into the low-pressure turbines, followed by a return of the aerated condensate to the boiler system, is a more probable cause.

T. L. B. Welb and J. D. Yoder<sup>151</sup> propose that the acid discharge from a cation-exchanger should be used for scale removing; the water will be free from metallic ions and will contain up to 200 p.p.m. of mineral acidity. Another agent<sup>152</sup> for scale removal which has been covered by a patent is a solution of sodium lignate from wood cellulose manufacture; an anti-frothing agent has to be embodied before use. H. Moll<sup>153</sup> has noticed that phosphate conditioned water favours the growth of algae in chemical plants, notably in condensers working at slightly elevated temperatures. He recommends that all industrial waters should be filtered and chlorinated before use in condensers if phosphate conditioning has been carried out. A patent<sup>154</sup> on the electrolytic descaling of boilers specifies the use of long flexible anodes carrying currents of about 300 amps. at 25 volts; the hydrogen evolved at the cathodic shell behind the scale develops a pressure sufficient to disintegrate the covering layers. Such currents would need to be carefully controlled to avoid localised action.

L. A. Burckhardt and C. E. Imhoff<sup>155</sup> have made X-ray analyses of typical turbine blade deposits. They have separated the components into (a) corrosion products from the blade metal, (b) water-insoluble compounds of calcium, magnesium, etc., (c) silica compounds and soluble salts. The deposits nearly all contain matter in group (c), with quartz as the most common pure substance. Many deposits contain up to 90% by weight of quartz, and these are in the form of a thin, firmly adherent scale. With these facts in mind, it is possible to assess the value of some cleaning methods for turbine blades which have recently been described.<sup>156</sup> These include changes of temperature, wet steam-washing and cleaning by chemical solutions. It would appear that drastic chemical methods will always be necessary unless more attention is paid to the removal of silica from the boiler feed. C. E. Imhoff<sup>157</sup> emphasises this, and proposes a maximum allowable content of silica in the steam of 0.1 p.p.m., corresponding to perhaps 5 p.p.m. in the boiler water. This is a content which can easily be obtained by ion-exchange methods as described above. It should be noted, however, that A. R. Mumford<sup>158</sup> thinks that much of the carry-over of solid with steam is due to film effects in the surface layers surrounding the steam bubbles, while

H. Bruckner<sup>159</sup> has reported sodium carbonate entrainment from over-softened water. The observations of Jacoby, Gunderson<sup>43,44</sup> *et al.*, reported in the heat transfer section, should also be consulted.

Deposits on the hot gas side of heating surfaces can be associated, according to H. E. Crossley,<sup>160</sup> with the presence of alkaline chlorides and a high sulphur content in the fuel used. A considerable reduction in deposit is noted if the coal is pulverised before use. Crossley, with A. Poll and F. Sweett,<sup>161</sup> then proceeds to show that the hot gases from pulverised fuel firing are rich in fine ash particles containing  $\text{Fe}_3\text{O}_4$  and unburned carbon. These, it is argued, will reduce the  $\text{SO}_3$  in the gas and check an initial attack on the heating surfaces which provides a lodgement for the following deposit formation. C. J. Gray and W. Kilner<sup>162</sup> have noted a troublesome tendency in modern crude fuel oils to form stable emulsions with sea water. These emulsions, fed to the oil burners, give alkaline vapours which rapidly attack the furnace refractories and also form sticky deposits on heating surfaces. These emulsions can be broken down fairly easily by the addition of wetting agents, such as "Teepol," in amounts up to 0.1% on the water involved.

### Plant design and control

A new form of high-pressure vessel, first constructed as a war-time improvisation, has been described by H. Birchall and G. F. Lake.<sup>163</sup> A thin shell of 1 in. steel plate is reinforced by a series of laminar rings, cut from ordinary 1 in. plate and fitted to the shell by shrinkage. These rings take up the hoop stress, while longitudinal forces are contained by another series of elongated oblong hoops, again of 1 in. plate, built into a "portal frame." Two large pressure vessels built on these lines have given satisfactory service at 350 atmospheres pressure. The method of construction gives no advantage over forged one-piece vessels, or over multi-layer wound construction, in the critical value of weight of metal per unit of reaction space, but it is relatively simple, with no large and costly plant requirements for fabrication. Only the end closures call for metal of thickness greater than 1 in. Large pressure vessels of this type will need careful handling in service and precautions such as those described by S. Scorer<sup>164</sup> will have to be observed. Design problems are simpler than in the reverse case of plant under external stress, as in vacuum practice. The American Society of Mechanical Engineers are attempting to establish a code for design in such cases. F. V. Hartmann,<sup>165</sup> in reporting progress, gives a series of charts for use in construction of vessels in steel, nickel and aluminium alloys, while different forms have also been presented by D. F. Windenberg,<sup>166</sup> and R. Storm and H. L. O'Brien.<sup>167</sup>

The qualities of a pressure-resisting gasket should be assessed, according to K. Wellinger and A. Stanger,<sup>168</sup> by testing the deformation under load, the permanent strain under a prolonged load, and making a determination of the air pressure required to bring about a fixed leak through a standard form of joint. An attempt<sup>169</sup> to control valve seizure when controlling the flow of corrosive chemicals entails the use of two seating surfaces, one for flow control and the other for preventing penetration to the

gland section. This allows the gland packing to be very loose, and a special wax-impregnated material is used.

Two more papers have appeared on the determination of true contact time in a continuous reaction system. H. J. Kandiner<sup>170</sup> follows previous workers fairly closely in the derivation of an expression for sampling lag in a number of mixing vessels in series. His equations allow for varying capacity in the various vessels, with a constant total volume of material passing. S. R. Brinkley<sup>171</sup> has taken up the case in which the volume of reactants varies, as in a catalytic gas reaction. He proposes a solution for the determination of contact time where the rate of reaction is not known.

A survey of the present position of instrumental control, read by J. W. Broadhurst, T. C. Broderick, A. W. Foster and G. E. Wheeldon<sup>172</sup> to the Institution of Electrical Engineers, suggests that pneumatic methods are best for power transmission, and that the main problems of control lie in the instrument used to measure the determining variable. E. S. Lee,<sup>173</sup> in a description of modern measuring instruments, stresses the merits of the mass spectrograph as a means for indicating, at one and the same time, the concentration of as many as eight components in a reactant stream.

D. M. Considine and S. D. Ross<sup>174</sup> draw a distinction between two control methods, of "ratio flow" and "cascade control." In the former a fixed ratio is maintained between two variables, while in the second a single variable is kept close to an arbitrary value. The use of a vapour-pressure bulb in the control of fractionating columns has already been mentioned in previous Reports, but an account given by G. G. Gallacher<sup>175</sup> may be of interest. The bulb, fixed in the liquid on one of the top plates, contains one of the components of the product, and a pressure lead to controls maintains the operation of the column to within very narrow limits. The latest addition to means of recording liquid levels in a closed tank is a radioactive float, registering on a Geiger-Müller counter. L. M. McCaslin<sup>176</sup> proposes means whereby this "Gagetron" can be used to control the level as well as indicate it, and points out that no connection or lead through the walls of the vessel is required. There are a number of competitive devices for this work of level indicating, as R. H. Munch<sup>177</sup> shows in a discussion in displacement type meters, while C. F. Cusick<sup>178</sup> has used differential pressure devices. It is possible,<sup>179</sup> by using diaphragm pairs of different sizes, to magnify pressure indications and thus obtain very accurate readings of liquid level. The long air lines for pneumatically operated valves are easily choked by deposits of moisture, oil, or dust. J. N. Franklin<sup>180</sup> proposes that these should be carefully removed from the air after compression by scrubbing, absorption, and cold traps; it may be possible to use Karbate rings and water lubrication on the compressor.

A photo-electric cell has been used<sup>181</sup> to control the setting of a knife peeling off solid and filter aid from a rotary filter. The white pre-coat must be exposed continually from under the filter cake, and the knife is advanced just enough to do this. Discoloration of a metal strip by water vapour has been used<sup>182</sup> in another unit to give a measure of the moisture content of a gas stream.

## Materials

The increasing use of rubber for all engineering purposes has called for knowledge of a wide range of physical properties. J. F. D. Smith, in listing these requirements,<sup>183</sup> has drawn up a bibliography of available references, but has pointed out several gaps in the data. The most typical use of rubber is in the lining of tanks, and C. C. Downie<sup>184</sup> has described recent developments in this operation, both for natural and for synthetic rubbers. When concrete tanks are lined with acid-resisting bricks, the mortar can conveniently be made up from a sulphur-synthetic rubber mixture applied in a molten condition, while expansion joints are easily made from un-vulcanised rubber sheet. Plastic linings are in active competition with rubber, but unfortunately the two most inert plastics, polythene and teflon (tetrafluorethylene) cannot be made to adhere to metal or any other material. This is due, according to E. B. Yelton,<sup>185</sup> to their extreme lack of reactivity, and he suggests that a teflon shell would make a good lining for a spray dryer, as no partly-dried fragments could adhere to the walls. Polythene can be flame-sprayed on to metal, but is very easily detached at corners, and can only be treated as a loose lining. A process for the inside coating of pipes with polyvinyl chloride, described by J. Rinse,<sup>186</sup> heats up the pipe by induced electric currents, and forces the resin coating into place by pressure. These pipes are stable to all but the most corrosive chemicals, and are comparable in price with Pyrex glass tubes. It may be noted that pipes and plant sections in an impervious resin-bonded graphite are now being manufactured in Great Britain.<sup>187</sup>

V. Evans<sup>188</sup> has given an account of the various acid-resisting cements now available, and gives instances of their use in floors, tanks and conduits. He hopes to see developments in the use of silicone resins, and some attempt made to control the polymerisation of polythene and teflon. J. Alibert<sup>189</sup> has tested various synthetic fibres in the manufacture of filter cloths. He considers that these cloths should be woven from long filaments rather than from short staple fibre. A series of short papers<sup>190</sup> in Chemical Engineering Progress have dealt with new materials for low-temperature insulation. There are now several cellular plastic insulations and a plastic glass mass available to compete with cork and glass fibre.

The growing world scarcity of lead is leading to a search for possible substitutes in the handling of dilute sulphuric acid. A series of short papers<sup>191</sup> in Chemical Engineering for May cover the use of plastics, rubber, and various special alloys. Ordinary rubber can be used at room temperatures for strengths up to 50%, while ebonites resist 25% acid up to boiling point. Synthetic rubbers show no great improvement on this, and butyl rubbers are perhaps the best. Normal stainless steels are of little use unless nitric acid is present, but a 25% Ni-20% Cr-Fe complex can resist all strengths at room temperatures. Only the expensive Hastelloy alloys show any sign of giving the wide range of resistance exhibited by chemical lead. The Chlorimet group of alloys (Ni-Cr-Mo), according to W. A. Luce,<sup>192</sup> show exceptional resistance to all dilute acids, including sulphuric and hydrochloric, even at boiling point.

The production and use of almost pure (93–99%  $\text{HNO}_3$ ) nitric acid greatly increased during the war, and a continued supply in peace time has led to some transport difficulties. G. A. Sands<sup>193</sup> reports the results of tests on welded steel and aluminium. Cold working of the metal did not increase corrosion, but the operation of welding tended to give localised attack just as with somewhat weaker acids. A final test was carried out with two drums, fabricated in stainless steel with columbium stabilisation, in which were stored 93 and 99%  $\text{HNO}_3$  respectively. These were exposed to sun and weather over a three-month period, and it was found that, provided spillage was avoided, attack on the metal was not marked. A fair pressure developed, and was gradually discharged through incidental leaks, while the acids were discoloured, especially in the case of the 99% liquid. A paper by N. Kaplan and R. J. Andrus<sup>194</sup> on the resistance of several metals to fuming nitric acid (containing  $\text{NO}_2$ ) and high nitric content mixed acid may be consulted, but the tests were of the normal laboratory type, with samples cut from rod or bar stock.

The Annual Review on Materials appears in *Industrial and Engineering Chemistry* for October, 1948.<sup>195</sup> The bibliographies are very extensive, so much so that the commentator on fibres has given up the struggle to review, and merely lists 273 references and titles. The review ends with a comprehensive tabulation of the properties of most common constructional materials, in which chemical resistance, physical properties, methods of fabrication and typical usage forms are all included.

### Oxygen production

A number of papers mentioned in the 1947 Report dealt with this branch of plant technology, which was sufficiently important for a Joint Conference of the Institution of Chemical Engineers and the Physical Society to consider the process. At these meetings, M. Ruhemann<sup>196</sup> pointed out the analogy between conventional distillation processes and the separation of oxygen from liquid air. He showed that conditions of operation were very rigidly circumscribed in the latter process, as all the cooling, to provide condensation and reflux flow, had to be provided by the air being treated. For thermal efficiency, this same air had also to provide heat for the reboiling at the foot of the column. This, he showed, made it necessary to use a double column, two pressure process for the separation of reasonably pure oxygen, and also fixed oxygen concentrations at the centre of the double column within a very narrow range. This in turn determined the number of plates and the allowable reflux ratio. Thermodynamic efficiency in any separation of this type involves as near an approach to reversibility as possible, or, in distillation, by a decrease in the reflux ratio and an increase in the number of plates. Such an approach is not possible in liquid-air distillation, and it is not possible to reduce the power consumption per unit of oxygen produced below a certain figure, which many modern plants have nearly attained. A low-pressure cycle, utilising expansion turbines between the two sections of the column, give a slight increase in theoretical thermal efficiency, but fixes still more rigid working conditions, so much so that it may not be possible to work the process on small plants, because of leakage-in of heat through the insulation. Unless some new process

which can discard the double column is evolved, the author considers that limits of cost reduction have almost been reached.

P. M. Schuftan<sup>197</sup> distinguishes between the manufacture of first grade and medium purity oxygen, and processes for enriched air. First grade oxygen of above 99.5%  $O_2$  is only required in relatively small quantities, and can be prepared by the original Claude process. Production of medium grade (85–98%  $O_2$ ) gas allows the use of regenerators, with a balancing of gas streams in various ways to ensure removal of deposited impurities. These regenerators approach more nearly to reversible working than tubular exchangers, while the working of the fractionating column grows simpler as the purity of the product decreases. As this grade of oxygen is required in very large quantities, small turbines can be used as expansion engines instead of the larger reciprocating types; this cuts down heat loss rather than improve power generation. Finally, if only enriched air of 80–85% oxygen is required, it may be possible to dispense with the double column working. A new process introduced by the British Oxygen Company, and using a subsidiary nitrogen circuit, will give medium grade gas with a single column. This last gives the lowest power requirement so far recorded—0.434 kWh. per cu.m. of 100% oxygen.

J. R. Park<sup>198</sup> considers the incidence of other charges besides power in the production of oxygen in a usable form. Distribution is always costly, whether cylinders or liquid gases are being transferred from plant to user, and the plant capital charges are high. The cost of erection of a plant to manufacture 300 tons of oxygen per day will be about half a million pounds, and smaller plants are relatively more costly. Many figures have been given for production which have omitted one or more of these indirect costs, while power charges are much higher in the British Isles than in the U.S.A. At a power rate of 0.6 pence per kWh., medium purity oxygen will cost in power alone about 7 pence per 1000 cubic feet, and this is some 60% of the total production cost. Any marked decrease in these charges is unlikely, unless some revolutionary process is discovered. However, the advantages of bulk production and use at a single factory site are very considerable. An interesting experimental oxygen plant built during the war worked on an absorption cycle, using "Salcomine"—a cobalt di-salicylal ethylene diamine. B. B. Fogler<sup>199</sup> thinks that a process worked on this basis might compete with standard methods for small outputs.

### Miscellaneous

A series of papers on Chemical Engineering Education were presented at the Congress of Pure and Applied Chemistry in July, 1947.<sup>200</sup> C. M. Auty considered that, for chemical plant design, graduates should receive the widest possible basic training, and should obtain as much works experience as possible during vacations. A. Guyer described the training of "Engineer Chemists" in Switzerland, and agreed that a good all round knowledge was more desirable than specialisation. W. M. Cumming and F. Rumford gave an account of the plant required in chemical engineering laboratories, and suggested that, in a course of this type, operation of the plant should be directed towards the elucidation

of a problem rather than a set experiment. H. C. Weber, in a paper published elsewhere,<sup>201</sup> described an "ideal" chemical engineering laboratory. The plant was so small that it could be moved round in a truck, and it is doubtful if such small units would give a reasonable grasp of industrial technique. A survey<sup>202</sup> of German training suggests that the chemistry departments of technical colleges were aligned to produce an "Engineer Chemist."

The present position of refrigeration practice has been reviewed by S. F. Dorey,<sup>203</sup> and he states that most large plants still work with reciprocating compressors. Some centrifugal compressors have recently been built in the U.S.A. for "Freon" plants. A comment on the working of centrifugal compressors by E. P. Palmatier<sup>204</sup> brings out the point that the speed of sound in these heavy vapours is very low, so that multi-stage working is necessary for relatively small pressure increases. The liquid evaporation should be in a series of steps matching the stage of compressor working, with vapour feed back at each stage. In these circumstances it is possible to obtain efficient working at  $-40^{\circ}\text{F}$ . Steel parts for these low temperatures should be made from a nickel-steel alloy. M. Ruhemann,<sup>205</sup> in an analysis of the ammonia absorption refrigeration cycle, compares the boiler and absorber with the exhausting and stripping sections of a fractionating column. He derives equations for heat and mass transfer and gives a pressure-temperature-composition chart for the ammonia water system. A patent<sup>206</sup> on refrigeration by the use of this cycle specifies a two-stage evaporation and a two-stage absorption.

In many chemical plants a high fire risk exists, and a special fire extinguishing system must be provided. H. W. Zussmann<sup>207</sup> describes the use of surface active agents in the water or foam used for fire fighting. W. F. Cooper<sup>208</sup> stresses the fire danger caused by static electricity accumulation and lists the precautions which should be taken to prevent sparking. Other fire precautions, described by G. B. James,<sup>209</sup> include the storage of all inflammable liquids in underground tanks and the comprehensive trapping of drains to prevent passage of heavy vapours.

N. T. Gridgeman<sup>210</sup> has noted applications of statistical methods in the chemical industry. He suggests simple methods for the use of statistics in experiment planning and quality control. This is also the theme of a book<sup>211</sup> published under the aegis of Imperial Chemical Industries, and giving an account of the way in which statistical methods are applied in their organisation. M. W. Thring<sup>212</sup> has made a study of the construction of small plants which accurately reproduce the operating characteristics of full-scale units. The same theme is taken up by R. C. L. Bosworth,<sup>213</sup> with special reference to the transfer of data on catalytic processes.

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# GAS, DESTRUCTIVE DISTILLATION, TAR AND TAR PRODUCTS

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THE year 1948 has seen the process of nationalisation of the fuel industries carried nearly to its conclusion. By the end of the year the coal industry has been under the National Coal Board for two years. Proposals for the revision of its administrative arrangements have been made both by a committee set up by the Board under the Chairmanship of Sir Robert Burrows<sup>1</sup> and by external commentators. It appears, however, that the Board will leave its carbonisation department under divisional control, forming a separate and self-contained branch of the N.C.B. This is not surprising since the annual report and balance sheet of the Board<sup>2</sup> showed that although a loss of £23,255,586 had been incurred during 1947, its carbonisation department had made a profit of £925,555 or 3s. 1.3d. a ton of coal carbonised.

The electricity industry has come wholly under the control of the British Electricity Authority, and the Gas Act, 1948, has become law. The Act sets up 12 areas, each of which is under the jurisdiction of an Area Board charged with the primary duty of developing and maintaining an efficient, co-ordinated and economical system of gas supply and coke production and of developing efficient methods of recovering products.<sup>3</sup> These Area Boards are virtually autonomous, constituting in effect 12 large gas undertakings. Their chairmen, together with independent persons as chairman and vice-chairman, form the Gas Council. This Council has extensive responsibilities in connection with the considerable financial affairs of the gas industry and obligations in respect of research, education, training and conditions of employment. The Council may be expected to represent and act for the industry, where the industry as a whole is affected, in the formulation of policy, labour relations, and certain other matters. The Area Boards are largely independent in the management of their affairs, but in developments involving substantial capital outlay, and in certain other matters must act under a general programme approved by the Minister and/or the Gas Council. A very important provision is that there must be consultation between the Area Boards and the National Coal Board, where the N.C.B. is operating carbonising plant in a Gas Board area; this should ensure orderly development of carbonisation to provide the necessary gas and coke with the minimum of overlapping.

The need for a national fuel policy has long been evident to fuel technologists, though the difficulties in devising a comprehensive and technically sound policy must not be underrated. It will require the wisdom of a Solomon to decide the place that should be occupied by carbonisation, electric power, raw coal in all its forms, etc., in a comprehensive policy designed to meet the fuel and power requirements of the

country at the minimum cost in coal, oil and money.<sup>4</sup> The Council of the Institute of Fuel has addressed to the Prime Minister and to the Minister of Fuel and Power a memorandum urging the necessity for formulating a long-term policy of co-ordination in national fuel matters, and suggesting that a Royal Commission or a high-level committee should be set up for the task. The reply has been given that it would not be possible to proceed with such a policy until all the major fuel industries had been nationalised.<sup>5</sup> That has now been done.

### Scientific Advisory Council

The Minister has set up a Scientific Advisory Council to examine the scientific aspects of many fuel problems, and has appointed a Chief Scientist to the Ministry. Some hint of what problems are likely to be examined may be found in a statement by the Minister.<sup>6</sup> On the domestic fuel side, the Government has accepted the Simon Report (which involves, *inter alia*, the abolition of smoke) as the long-term plan for improving the utilisation of fuel in houses. On the issue of co-ordination of production and consumption of fuels, the Minister has said :

"Some feel that there might be advantages in locating power stations at or near pitheads, or combining gas-works and power stations. Some feel that underground gasification of coal has great possibilities, particularly if associated with the gas turbine for generating electrical power. All these and other proposals for co-ordination involve scientific, economic, social and strategic problems of the greatest difficulty and complexity, and will require most careful study."

The need for a national fuel and power policy is related to our present difficulties as a nation, but is also consequent upon the growing realisation that our coal reserves are nothing like so extensive as was formerly imagined. It has been estimated<sup>7</sup> that the life of our coalfields is likely to be about 160-200 years at present and planned rates of output. This problem does not affect only Britain. It is commonly believed that coal reserves in the U.S.A. are sufficient to last at the present rate of use for anything up to 4,000 years. Andrew B. Crichton<sup>8</sup> has now suggested that the American estimate may well be very much too high and the total American reserves may not be more than sufficient at present production rates and losses to last for more than 250 years. In the highly industrialised East, where 92% of the coal is produced and used, the estimate was put at only 90 years' supply. The coal industry of U.S.A. has been so destructively competitive that much coal has been lost in mining that could have been recovered for a few extra cents a ton. Coal mines have been abandoned for economic reasons resulting in the loss of millions of tons of coal, most of which could not now be recovered because of the prohibitive cost. There is a growing shortage of low-sulphur coking coal in the U.S.A.

The period of prodigal use of world fuel reserves has come to an end everywhere—or nearly everywhere—and economy and efficiency are the pass-words from now on. In this the scientists and the technical men enter into their kingdom. G. M. Lees<sup>9</sup> has suggested that the combined

proved and possible oil reserves of U.S.A. will be exhausted within 20 to 40 years, and that the world oil reserves will not suffice for more than about a century at the rate of consumption likely to be required by the present rapid increases in mechanisation. Consequently, the U.S.A. is spending large sums on research, including pilot plants, and on the production of oil from coal, a step that will further reduce world coal reserves.<sup>10</sup>

## Carbonisation

The time taken to collect and analyse statistics generally causes them to be a year out of date. The *Statistical Digest* of the Ministry of Fuel and Power, issued at the end of 1948 gives statistics to the end of 1947. In that year, 171.7 million tons of coal were used in Great Britain, of which 19.8 million tons were carbonised in coke ovens and 22.7 million tons in gasworks. Each year from 1940 onwards has seen a substantial increase in the quantity of town gas sold, in spite of the difficulty of securing new plant. In 1947, the total gas available at gasworks was 2,310 million therms, of which 11.1% was bought from coke ovens. Two-thirds of this was supplied to domestic consumers, 18% to industry, and the rest to shops, offices, Government departments and other similar consumers. The coke produced was 26.25 million tons at coke ovens and gasworks combined. The coal carbonised at gasworks was distributed among the various types of plant as follows:

	Tons
Horizontal retorts .. .. .	9,381,508
Continuous vertical retorts .. .. .	10,892,957
Intermittent vertical retorts .. .. .	1,547,623
Other plant, including coke ovens .. .. .	589,634

A small quantity was also used for the manufacture of water gas, producer gas and for complete gasification.

## Low temperature carbonisation

A comprehensive account has been published of the Disco plant at Pittsburgh, Pa., said to be the largest low-temperature coal distillation plant in the world.<sup>11</sup> This system involves prior oxidation of the coking coal in air for 2 hours at 370° C., followed by carbonisation (often being mixed with breeze from a previous charge in a rotary retort) starting at about 370° C. and increasing in temperature to 450° C. The final product is principally in the form of balls 1 to 8 in. in diameter and containing 15–17% volatile matter. The yields from a short ton of coal (2000 lb.) are: "Disco" smokeless fuel, 1440 lb. (72%); gas (of 375 B.Th.U./cu.ft.), 3700 cu.ft.; crude tar, 15 gallons. A general account of oxidation and pre-heating systems (of which the Disco process is one example) has been given by John Roberts,<sup>12</sup> and it is there concluded that both the Disco and the Koppers medium temperature process are essentially blending processes and that pre-heating, with or without oxidation, would be unnecessary if a suitable inert material were available for blending.

An Italian low-temperature plant has been described by F. Roma<sup>13</sup> based on the principle of internal heating by external combustion; the

coal is treated in a closed retort and internally heated by contact with a current of the gases generated in the retort, operating in closed cycle and periodically reheated in a separate heating unit. It is used at present for producing oils from poor-quality fuels, including carbonaceous rocks, and seems to be primarily designed for shale oil distillation, though it can apparently be used on non-coking coals. High yields of oil are claimed.

### Oil shale distillation

A detailed account has been published<sup>14</sup> of the mining, retorting, and refining practices adopted for the recovery of oil from Scottish oil shale. The output of oil shale reached a maximum of  $3\frac{1}{4}$  million tons in 1913, but is now down to  $1\frac{1}{4}$  million tons obtained from 12 mines. The raw shale is retorted at four crude oil works and the crude products are refined at Pumpherston; there are also two sulphuric acid works, a candle factory and a modern brickworks using spent shale for the manufacture of bricks. At the Westwood crude oil works the shale is crushed below 4 in. in size before being heated in the retorts. There are two benches each of 52 retorts capable of dealing with 1040 tons of shale a day. The retorts, each of 10 tons capacity, are 34 ft. high, the upper 14 feet section being in case iron, elliptical and tapering from the base upwards. The lower 20 ft. is built entirely in brickwork. The retorts operate at  $550^{\circ}\text{C}$ . in the top section, increasing to  $1000^{\circ}\text{C}$ . in the brick-built lower section. The spent shale is water-spray-cooled, and the steam thus generated, supplemented by steam injectors, is used for retorting the shale. The average yield is 20 gallons of crude oil, 3.5 gallons naphtha, and 30 lbs. sulphate of ammonia a ton. Steam and air are injected into the bottom of the retorts. The steam is used to prevent cracking, to distribute the heat in the retort, and to form water gas and ammonia with the spent hot shale; the function of the air is to assist the heating by combustion with the carbon in the shale; heating is therefore both internal and external. Waste heat boilers are used to extract heat from the external heating gases.

The gas from the retorts is cooled and condensed to remove oil and ammonia liquor, scrubbed with water to remove ammonia, and with gas oil to recover light hydrocarbon vapours. Every possible advantage is taken of the use of waste heat. The refinery plant produces motor spirit, solvent naphtha, diesel oil and paraffin wax. The crude oil is distilled in a pipe still and the fractions are separated in the usual way. The heavy residue in the pipe still is treated in coking stills, the distillates being returned into the crude products and the coke sold for the production of electrodes. The next higher boiling product, wax-bearing oil, is cooled to allow the oil to crystallise, the cooled oil being pumped through a series of filter presses where the wax crystals are deposited; the wax is sweated to remove further oil and decolourised by passing it in the molten state through a vertical column of bleaching earth. The wax-free oil along with the oil from the wax filters is redistilled in a pipe still to obtain crude motor spirit, diesel oil and a heavy residue. The residue is put through a cracking plant in which it is converted into motor spirit and disesel oil. Crude motor spirit is redistilled in the usual way. All gas

evolved from the various distillation processes is collected and used as fuel, after being washed for removal of light spirit. From the spent shale, bricks are produced with a crushing strength of 3500 lb./sq. in.; the spent shale is pulverised, mixed in a pan mill with hydrated lime and lime slurry, the mixture passing to a moulding machine and thence to steam-heated ovens or autoclaves in which the bricks are hardened by treatment with superheated steam for eight hours.

### Coke oven practice

Due to local shortages of supplies of coking coals, there have been repeated attempts to use non-coking coals for the manufacture of metallurgical coke, or for the direct production of pig-iron from ore. P. Lameck<sup>15</sup> has described the production of pig iron using low-grade ore or fines by a process of briquetting invented by Ludwig Weber. The ore is mixed with sufficient coal to smelt it and after adding a binder (coal tar pitch or sulphite lye) the mixture is briquetted by a roller-press into ovoids which are carbonised at between 550 and 600° c. followed by smelting in a low-shaft furnace. The proposal has been made to use oxygen instead of air blast in the smelting operation, thereby producing a gas of higher C.V. containing a much lower proportion of inerts, to enrich it with hydrocarbons so that it can be used for town purposes.

A. Thau<sup>16</sup> has described the Didier two stage process for which the claim is made (supported by practical trials) that it will enable first class metallurgical coke to be made from non-coking coals and even from lignite. Non-coking coal below 2 in. in size is carbonised at 550–600° c. to remove tar. The normal continuous vertical retort can be used for this purpose. Gas is admitted at the base of the retort to increase heat transfer and prevent decomposition of the tar. The semi-coke is cooled, crushed and mixed with 5–8% of the pitch produced from the low-temperature tar from a previous operation and with 10% of coking coal. The mixture is briquetted at 0.65–1.3 tons/sq.in. and the briquettes carbonised in continuous or intermittent vertical chamber ovens at 900°–1000° c. The mixed gas from the two retorts has a C.V. of 480 B.Th.U./cu.ft. It is claimed that the cost is only slightly greater than the cost of making metallurgical coke in a normal coke oven plant.

A detailed account of the effect of coke quality on British blast furnace operation has been given by D. Joyce.<sup>17</sup> The amount of coke required is in the first place in direct relationship to its carbon content, and therefore in inverse relationship to its content of ash and moisture; moreover, the additional slag arising from higher ash content requires additional carbon to melt it. Since the rate of coke burnt at the tuyères is limited, additional ash reduces the output from the furnace. High carbon and low ash content are thus the first requirements. It is better to provide a coke with constant ash content, even if high, than with ash content varying considerably from day to day, since variations in ash content can quickly bring about a change in slag volume and/or slag formation with subsequent change in the analysis of the iron produced, especially its silicon content. Since 90% of the sulphur charged into the furnace comes from the coke, the more economical a furnace is in coke

consumption, the less sulphur it has to carry. The lower the sulphur in the coke charged, the more economical furnace operation becomes; lower sulphur coke permits the use of leaner slags, less limestone additions, more rooms for ferrous materials in the charge, increased production and lower coke rates. Sulphur can be removed by using excess lime, but as lime has a high m.p. ( $\text{SiO}_2$ ,  $1710^\circ$ ;  $\text{Al}_2\text{O}_3$ ,  $2050^\circ$ ;  $\text{CaO}$ ,  $2500^\circ$ ;  $\text{MgO}$ ,  $2100^\circ$  C.) sulphur will require extra coke for melting the slag since the maximum normal furnace temperature is around  $1760^\circ$  C. If the furnace is operating on a slag with a formation temperature above that of the furnace temperature, the tendency will be to deposit lime on the hearth, with serious furnace derangement. All the phosphorus charged into the furnace is completely reduced and enters the iron. High moisture content involves the furnaces in paying for water at coke prices. On foreign ore practice, coke occupies about 55% of the volume of the furnace and much depends upon the physical quality of the coke to maintain voidage in the furnace stock column to promote even furnace driving to aid distribution and to obtain intimate gas-to-ore contact. Reduction in the permeability of the column to gas may result in "hanging" and deterioration of furnace operation. Combustibility too is important; coke of good combustibility, burning rapidly at the tuyères, furnishes the necessary rapid shrinkage for rapid furnace movement, and at the same time develops the necessary temperature head in a comparatively small area. Breeze has no fuel value in the blast furnace, and tends to reduce the permeability of the stock column.

E. G. Gardner<sup>18</sup> on the strength of extensive plant scale investigations in which selected coal blends were carbonised under identical operating procedures and were tested on one blast furnace under conditions as nearly identical as possible, has concluded that the conventional physical tests on coke are a satisfactory yardstick for measuring differences in the quality of the coke and their influence in the blast furnace.

S. Weiss<sup>19</sup> has stated that present coke oven capacity in the U.S.A. is roughly 76 million tons of coke (110 millions of tons of coal a year); about 20% of this has been constructed within the last five years and and about 50% consists of ovens over 20 years old. Good coking coals are in short supply and vigorous action to conserve such coals is urged. There is no shortage of metallurgical coke in America, but other countries have a different story to tell. Shortage of metallurgical coke in France is a serious obstacle to iron and steel production and suggestions are made for a considerable increase in the number of coke ovens in that country. P. Georges<sup>20</sup> holds that France should carbonise 27 million metric tons of coal and states that if this programme were adopted it would be necessary to erect 3200 new coke ovens in addition to the 1400 at present in operation. The present total of coal used for carbonisation at gas works and special ovens is about 4 million metric tons.

The Monnet plan drawn up for the rehabilitation of French industry deals with coke only in a summary way. Hard coke was produced in France originally mainly to get rid of coking fines and was insufficient to meet all needs. The resulting import of coke was not considered to be satisfactory on either economic or strategic grounds. Therefore attention has been given to producing good cokes by blending, and it

is planned to build 25 coke oven batteries each to carbonise 1500 tons of coal per day, thereby doubling France's metallurgical coke output.<sup>21</sup>

In Britain, special efforts have been necessary to produce the requisite coke supplies for the furnaces. The major problem is whether those supplies can be maintained in future years. Due to a variety of causes there has been little new construction since the war. It has been expected that orders would be placed in 1948, but that has not been done. Concern lest plants now becoming elderly or old should fail before they have been replaced has been expressed by R. J. Barritt.<sup>22</sup> The expectation of life of a modern silica coke oven is 90,000–100,000 tons of coal carbonised; on this estimate it is calculated that a total requirement of 22 million tons of coal carbonised a year requires a replacement rate of 230 ovens a year over the whole country, and, in fact, during 1932 to 1930 this was about the rate at which new ovens were built. During the war years the building rate fell to well below 100 ovens a year and this "deferred maintenance" requires that another 600 ovens be built. Abnormal damage due to war operation (e.g., black-out working conditions) accounts for another 300 ovens that urgently require rebuilding. If these arrears are to be cleared off in, say, 6 or 7 years, the rate of building must increase to 350 ovens a year. In practice, ovens built and orders placed during 1948 have been very far below what is required by this programme and in view of the pressure upon plant constructors, including the manufacturers of motors and other ancillary machinery and in particular the shortage of silica bricks, it seems doubtful whether some of the batteries will last out until new ones have been built to replace them. It is understood that large orders are likely to be placed by the Coal Board during 1949. The shortage of silica bricks is not due to causes that the brick-makers should have foreseen in advance.<sup>23</sup> There has been competition between them and the N.C.B. for clay miners; production is said to have been reduced through the poor quality of coal supplied for the kilns; the refractory material industry, however, has a high priority for labour, materials and fuels. In 1935, the industry manufactured 206,000 tons of 95% silica products; over the years 1947–50 it is expected to produce 269,000 tons, of which 210,000 tons will be allocated to the steel industry, 45,000 tons to the carbonisation industries (gas works and coke ovens), leaving 14,000 tons for sundries and export. To build 350 all-silica ovens a year would require about 35,000 tons of silica a year, leaving very little for the gasworks. The replacement rate average of 230 ovens a year could be maintained, however, and leave enough for gas retorts.

A contribution to the problem of prolonging the life of existing oven batteries has been made by H. Kerr and A. Taylor.<sup>24</sup> This paper emphasises the importance of efficient maintenance and good operation. Rate of working, and particularly the carbonising temperature employed, have an important influence on the life of the bricks. In ovens fired with low-grade gas, every care must be taken to clean the gas from dust to a high degree. The pressure in the collecting main is important. Failure of oven ends, comprising spalled jamb-bricks, slagged oven walls and bent buck-stays are likely to be caused by "stickers" (coke that proves difficult to discharge). Self-sealing doors may give rise to defects which influence this form of damage. Ash or slag may attack the walls when

the ovens are operated at high temperatures and the ash is fusible. This arises from coke burning away between discharging and recharging an oven. Coal may also lodge in joints, and burn away, leaving the ash to attack the jointing material. Excessively long standing of ovens empty and under fire should be avoided. Coarse wet coal carbonised at flue temperatures above  $1300^{\circ}\text{C}$ . has been found to cause erosion in South Yorkshire but the reason is not clear. It is suggested that the damage only occurs with very wet coal, that the internal pressure of the gases breaks through the plastic layers at their weakest points, and that these weak points will be where the coal is least dense. Water already in the centre of the charge with additional water evaporated and condensed there will then drain down carrying salts which may attack the brickwork. This explanation appears to account for the mode of occurrence of the damage, but cannot be regarded as proved. Headers in ovens operating in South Wales are found to spall; no opportunity has yet occurred of examining these bricks when cold, but the cause is almost certainly mechanical and may be due to the swelling pressures developed in low-volatile coals (to be discussed later). The suggestion is made that ovens should be built in small batteries to permit letting down smaller units more readily for repairs. Walls should be sufficiently solid to resist slight pressures and the ends should be able to stand up to the repeated shock of removing and replacing the doors.

The problem of designing a silica oven which can be repeatedly allowed to become cold and reheated without damage is claimed to have been solved by D. Petit of France.<sup>25</sup> This is an oven of which the walls are constructed in silica and the lower portion in semi-silica. The walls are divided vertically into 12 or 13 pillars each 1 metre in length; the pillars are not tongued and grooved but are built with plane expansion joints between them of a width based on the known expansion of the silica so that on heating they close up to give a solid wall. Carbon impregnation completes the joint and makes the walls gastight. Batteries of these ovens are under construction in France and the author has given details and photographs of his construction, based on the operating results of the pilot battery built at Pont-à-Vendin.

Damage has been occasioned in coke oven plants (and possibly also in gas retorts) through excessive pressure occurring in the charge during carbonisation. This damage may be sudden and catastrophic in character causing immediate disruption of the brick-work, but it is suspected that the same cause, less violently applied, may cause slow deterioration. An experimental Russell oven, in which a charge of 400 lbs. of coal is heated from two sides as in the coke oven at a flue temperature of  $1350^{\circ}\text{C}$ . has been built at Pontypridd by the British Coke Research Association, who have described the outcome of two year's work on this test plant.<sup>26</sup> One of the walls of the oven is fixed and the other can be moved on rails but is held in position by a weighted, balanced lever, through which the transmitted pressure of the charge can be registered. In general, serious pressures are developed by highly coking coals containing about 25% of volatile matter on the dry ash-free less  $\text{CO}_2$  basis. Coals are of three types: (a) those developing very little pressure in the test oven, (b) those developing a pressure of about 1 lb./sq.in. during most of the

period, with a much higher peak during the few minutes during which the plastic layers are in contact and before their conversion into semi-coke, and (c) those which in addition to showing the transient peak just described also develop pressure up to 5 lb./sq.in. and more during the rest of the period. Coals of type (c) are the most likely to give trouble, but in the absence of precise information it is difficult to interpret the results of the test. The higher the bulk density the greater the tendency to develop pressure. Width of oven has but little effect. The results on the effect of temperature were not conclusive because the lowest rate of heating was well above the rates used in practice. The best method of dealing with possibly difficult coals is to blend non-coking material higher or lower in volatile content, and to keep the bulk density as low as possible by fine grinding, addition of water and careful charging. It is found in practice that low flue temperatures are also desirable with certain coals, principally those which do not contract on heating the fully-formed coke in the oven.

### Future technical policy

The future technical policy of the carbonising industries has been discussed by G. E. Foxwell.<sup>27</sup> It is concluded that the primary purpose of coal carbonisation must be to convert coal into coke and gas, both of which are then used to better effect than raw coal. The production of chemical products is a secondary purpose of carbonisation. Increased supply of coke and gas to the domestic consumer is likely to become of primary importance in the light of the Simon report. The need for providing coke of the right quality and of meeting peak loads for gas and other fuels in the best way indicates that there must be close connection, possibly joint carbonising boards, between the coke ovens and the gas industry. It is unlikely that the production of oil from coal will be economic in this country so long as reasonably adequate supplies of natural petroleum exist. Jet propulsion may have a bearing on this and the coal-dust engine may create a demand for special fuel in the more distant future. It is not regarded as desirable for nationalised industries to undertake on an extensive scale the working-up of by-products when existing, efficient industries are doing this. There are, however, gaps which the nationalised carbonising industries may find it necessary to fill, ammonia and ethylene being possible examples. Linkage of coke ovens or gasworks with chemical works using the gas at such times as there is a surplus is not an attractive method of disposing of surplus gas. Chemical utilisation of gas for production of ammonia or methyl alcohol is unlikely to be developed further in this country and seems to require in general that the gas shall be low in price. The iron and steel industry is likely to produce up to 75% of the coke it requires, leaving other coke ovens to produce the remainder; this may vary between 2 and 3 million tons of coke a year—a fluctuating load that may be expensive to produce. Coke ovens other than those situated at iron and steel works will be essentially a part of the gas industry so far as their functions are concerned—even though owned by the N.C.B. The prospects for producing gas economically by pit-head carbonisation are slight except in districts where several pit-head plants are linked by a grid and spaced only a few

miles apart over the area and serve a populous industrial district. Long-distance gas transmission is only economic when gas alone is supplied and not when coke has to be transported over the same distance in roughly the proportions now supplied by the gas industry.

A. C. Middleton<sup>22</sup> has claimed that the first occasion upon which coke oven gas was used for town purposes was at Brissworth in 1905, when the village was wholly supplied by gas derived from a battery of Simon-Carves waste heat ovens at Rotherham Main colliery.

### Gasworks practice

Nationalisation is almost certain to have a considerable influence on British gasworks practice. It is likely that the smaller works will be supplied with gas from large central works, where it is economic to do so. The staff of the smaller undertakings will receive more help from senior headquarters staff of high calibre and in general it may be expected that the pace of application of new discoveries will be more rapid since the Area Boards will be more ready to accept responsibility than the individual gas engineer and manager, handicapped by the limited resources of his undertaking. On the other hand, the fear has been expressed<sup>69</sup> that the number of opportunities for experiment on a working scale will decline in future, not only because of the smaller number of gas-making units, but also on account of the increased size of those units which will cause plant-scale experiments to be more costly. In future, it is feared, fundamental modifications will only be introduced as the result of organised research, the openings for the application of new discoveries will be fewer, and the discoverer will be proportionately handicapped in proving any points on the technical scale.

With the change in the existing order of things, papers were arranged for the annual meeting of the Institution of Gas Engineers which should give a picture of technical progress prior to nationalisation. T. C. Finlayson and F. S. Townend<sup>29</sup> discussed gas production in perspective. Fuel economy is now regarded as of the highest importance. Figures in therms/ton of coal carbonised were given in this Annual Report last year (p. 32). One of the most promising directions for further fuel economy (in addition to the recovery of heat by dry-quenching the coke, which is not secured without some difficulty and expense) is by proper co-ordination of process steam and power requirements of the gasworks. Attention may here be directed to a very useful work on this subject by O. Lyle.<sup>30</sup> The choice of declared calorific value has been left to the individual undertaking in the past, but of the total gas made, 30% was of 450 B.Th.U./cu.ft., 11.6% of 475 B.Th.U. and 33.7% at 500 (this last due to the preponderating influence of one undertaking). A concise summary of the characteristics of the various types of gasmaking plant was contained in this paper. The conclusion was reached that the gas industry must remain a two-fuel industry, the major winter peak demands for heat being supplied by solid fuel, and that while the consumption and production of gas and coke must be balanced, any sale of gas at the expense of coke will leave unsold coke for which a market must be obtained as remunerative as that from which it was displaced.

There has been much interest during the year in the use of mechanical

producers for heating gas retort settings. This practice was originally devised by H. Koppers in Germany about 30 years ago, but in this country the Manchester Corporation gas department has taken the lead in applying the method to large-scale work, though H. Koppers installed a plant at the Whaley Bridge gasworks about 1926. R. Walker<sup>31</sup> has described recent development at Manchester in heating horizontal retorts by mechanical producers. The principal features of this practice are described. The producer gas is of more consistent quality than with step-grate producers, and the quantity of gas produced can be more easily adjusted; the pan-ash contains combustible matter amounting to  $\frac{1}{2}$  to 1% of the total carbon charged, as compared with a reject of 5 to 6% in step-grate practice; working conditions are easier and better, and the results are less dependent on the human factor; the retort house can be kept much more free from dust and dirt; settings can be started up from the cold with much less consumption of fuel and much better control over the rate of temperature rise than when using the normal method; the heating plant is more flexible and there is better control over the quality of the coke used and its effect on the heats; the life of the settings should be increased owing to more even heating, freedom from corrosive attack of ash, and the relative freedom from dust. The major advantage under present conditions is that it is very difficult to find suitable men to look after the step-grate producers and who are willing to do the clinkering and similar hard physical jobs conscientiously. As against these desirable features, mechanical producers involve higher capital costs and there is the loss of the sensible heat of the coke, and to some extent of the producer gas. Higher capital costs are compensated by decreased labour requirements and with good insulation the loss of heat from the gas need not be considerable.

At Liverpool Gasworks, mechanical producers have been applied to heating vertical retorts.<sup>32</sup> Three automatic 9 ft. diameter power gas producers are there in use for heating a 3 million cu.ft./day installation of West's continuous vertical retorts. Modifications were made to the producer to permit of the maintenance of a gas temperature of 400–430° c. in the main flue leading to the retort setting. The existing eight step-grate producers were removed to make room for the new installation. The producer-gas machines had automatic coke feeding gear, mechanical ash extraction, and each rated at 165,000 cu.ft. of producer gas an hour when using graded coke. Combustion chamber temperatures on all 33 in. retorts was satisfactory but certain difficulties regarding coal travel caused opinion to be reserved on the 85 in. retorts. A fourth producer has been installed and a 6 million battery of continuous vertical retorts were expected to be in operation early in 1949 fired by mechanical producers. In addition to the special features already mentioned it is pointed out that mechanical producers are under better control and can be fully instrumented, while standby plant can be installed which enable repairs to be carried out to the producer plants without reducing the production of gas.

Another example of mechanical producers for heating gas retorts is the plant at the Sydenham works of the South Suburban Gas Co.,<sup>33</sup> where coke breeze varying between 0– $\frac{1}{2}$  in. and 0– $\frac{3}{4}$  in. has been used to make

producer-gas in two 10 ft. 6 in. power gas generators, the gas being used for heating horizontal retort settings. Trefois mechanical producers coupled to a simple gas-washing plant have been used for this purpose at this works for 10-12 years but require the removal from the breeze of most of the material below 3/16 in., chiefly because of the restricted grate area and segregation in the producer. It is claimed that when using breeze at 30s. a ton producer gas is manufactured at 3.66d. a therm whereas with breeze at 20s. a ton the cost is 2.96d. a therm; 171.7 therms of gas are made per ton of wet breeze with a cold gas efficiency of about 73%. The breeze contained 14.9% of water, 14.6% of ash and 40% of it was below 1/4 in. in size.

The future possibilities of the methods of gas manufacture have been examined by A. R. Powell primarily for American conditions.<sup>34</sup> The carbonisation of bituminous coal in large ovens, supplemented by production of carburetted water gas, is regarded as the important gas-making method of the future. On economic grounds it is desirable to situate gas-making units near the centre of consumption rather than at the pithead. Low-temperature carbonisation is of no interest for economic gas production. The thermal efficiency of production of C.W.G. is likely to be raised by the use of oxygen. It is unlikely that producer-gas will be distributed generally, on account of its low calorific value. None of the processes of complete gasification so far proposed is entirely satisfactory; the most promising is said to be that in which a steam-oxygen mixture reacts with a suspension of powdered coal at high pressure (see later). For town gas production, underground gasification has little prospect. The combination of synthetic processes with gas manufacture seems unlikely to assist materially the economics of gas manufacture.

The low load factor of manufacturing plants that produce town gas for space heating has been the subject of an address by F. M. Birks,<sup>35</sup> who has also pointed to the effect of this and other considerations on gas tariffs.<sup>36</sup> Temperatures in England are such that the load factor may be as follows:

Base temperature level to be maintained by an appliance	Load factor of the appliance
65° F.	31%
50° F.	11%
30° F.	0.1%

The capacity required to produce this gas would presumably operate at an equally low load factor, with the result that the gas is costly to produce. The foregoing figures are also significant when applied to district heating. They show the low load factor at which self-contained district heating plants must operate. Moreover, "at least one recent district heating project was designed to raise the temperature of premises to 65° F. only when atmospheric temperatures were above 30° F., implying that some other fuel service, such as gas or electricity, would have to provide the heat for the temperatures below 30°, at the disastrously low load factor indicated." On the tariff question, it is clear that the costs of production will vary with the load factor imposed by a particular consumer's load, but since each consumer will generally be one of a group,

it is the load for the group which dictates the cost. A preliminary method is to allocate loads under (i) the portion affected by the seasons, and (ii) the portion that remains sensibly constant throughout the year (base load). Each of these has its (different) effect on costs. Uncertainties in basing a tariff on these allocations are the reaction of the consumer to the tariff (since it is the *future* consumption that is to be charged) and the inflation of monetary values, which has been going on for hundreds of years. The gasholder enables short-period loads on the manufacturing plant to be smoothed out. The diversity of the load also has an important bearing on the load as a whole.

In an attempt to provide plant capable of producing gas economically to deal with short, occasional, peak demands, *e.g.*, due to very cold weather, a process based on D.T.A. Townend's work on "Combustion" has been devised by the Gas Light and Coke Company.<sup>37</sup> The relationship between this process and D. T. A. Townend's work on combustion of hydrocarbons has been discussed by G. E. Foxwell.<sup>38</sup> The process is based on the partial combustion of petroleum oil under conditions in which the "cracking" flame coalesces with the "cool" flame. Air, heated to 380–400° C. and gas oil are introduced into a reaction chamber which is heated to 400° C., under conditions leading to very rapid mixing. Partial combustion occurs using up all the limited supplies of oxygen and with production of gas containing about 60% of N<sub>2</sub> and 11–17% of hydrocarbons and with a C.V. between 400 and 550 B.Th.U./cu.ft. according to the conditions. The plant is thermally inefficient but can be used economically for these very occasional peak loads.

E. A. Laundry and L. Muir Wilson<sup>39</sup> have described the modern development of the Congdon scrubber standpipe system as developed by the South Metropolitan Gas Company. The gas immediately on leaving the retorts is sprayed with ammonia liquor. This system enables slight pressure to be maintained in all mouthpieces during the whole carbonising period, individual retorts to be cut off both when discharging and when scurving, more regular pressure to be secured through elimination of wet seals, elimination of the governors, hydraulic mains, tar bottles and dip pipes on the top of the setting, the governors being replaced by a single automatic governor for each section; working conditions are cooler and much improved, stock pipes and heavy augering are largely eliminated.

W. Zankl<sup>40</sup> has found that the gas yield from the carbonisation of wood can be doubled by causing the gas to traverse the hot charcoal accumulated either in the carbonising chamber or in a neighbouring retort which has reached a later stage of carbonisation. Owing to its high density, the wood gas must either be mixed with coal or washed to remove CO<sub>2</sub>. P. Schenk<sup>41</sup> has found that the simultaneous carbonisation of coal and wood in a gas plant almost invariably causes the formation of a tar with high water content, strongly emulsified, and difficult to handle.

W. L. Boon<sup>42</sup> so long ago as 1934 drew attention to the importance of reducing as far as possible the production of breeze during the operation of breaking coke to produce certain marketable sizes. As a typical average figure, he indicated the degradation to breeze of 35% of the original make of coke to produce 65% of high-value product. The

importance of coke in the economics of gas manufacture has at last stirred the gas industry to begin research work, through the Gas Research Board, into the breakage of coke. Preliminary experiments have been made on a two-roll breaker by V. T. Taylor and D. Hebden.<sup>43</sup> This preliminary work indicated that screens should work at high efficiency in order to separate the maximum amount of the smaller sizes which must otherwise be produced by deliberate breaking. The rolls must be set correctly in such a way as to give the minimum of breeze (this is obtained at the widest setting) with the desired proportion of the smaller sizes. The difficulty of knowing what the setting should be has been largely overcome by the discovery that on putting a small batch of 30–40 lb. of coke through a commercial breaker, results are obtained almost identical with the bulk from the whole production under the same conditions of roll setting, etc.

A comprehensive survey of past work at Birmingham Gas Department on the quality of open-grate coke from continuous vertical retorts has been published by T. F. E. Rhead and E. T. Pickering.<sup>44</sup> Ease of combustibility of the domestic sizes of coke is affected mainly by the quality of the dry coke substance, size grading and the moisture content. The type of coal carbonised has the predominating influence. Carbonising conditions other than temperature do not exert much influence, but it is not regarded as desirable to produce a combustible coke by retaining volatile matter in it. Ash in the form of "bats," which may become "explosive" and damage furniture and carpets, is highly deleterious; Birmingham work suggests that the cause of the decrepitation is the bursting effect of steam introduced during quenching, and not the release of internal strains. It is recommended that to produce a good domestic coke a coal should be selected that by its constitution will yield a coke of high combustibility; the coke in the retort should be steamed (15–20% of steam being used); moisture should be kept below 5%; the ash content should be as low as possible with bats kept out altogether; the size grading will depend on the coal in that for the coals giving the most combustible coke fairly large sizes can be used, but for the less satisfactory cokes the material should not contain more than 30% above 1.5 in.; coke should be debreezed immediately before loading for delivery; and coke used for "coking-up" retorts after scaling (*i.e.*, coke which has, in effect, been heated twice over in the retorts) should be kept out of the open-grate coke hopper altogether.

Interest has been taken during the year in the application of the Oldbury chain grate stoker to burning coke breeze sized  $\frac{3}{4}$  in.–0. This is a chain grate stoker sufficiently small to be applied to Lancashire and similar boilers. It is stated that with a stoker having a grate area of 20 sq. ft. per flue it is possible to obtain an output of 6000–7000 lb. of steam per hour from a standard 8 ft. diameter boiler with a burning rate of 25–30 lb./sq. ft. and without any excessive carry-over of fines, whilst the output can be reduced to half this amount without difficulty.

Details have been published<sup>45</sup> of an experiment in communal grass drying undertaken by the Milk Marketing Board in collaboration with I.C.I. Ltd. at Thornbury. I.C.I. dryers were used for drying gases from a number of small farms in the vicinity. These dryers burn coke to

provide hot air which is circulated through the grass in the dryer. The semi-producer furnace is used in this machine, in which producer gas is made in the furnace and is burnt at the back of the furnace in two flues with excess secondary air so that a mixture of drying air and flue gases is passed at 140–150° C. directly to the grass, the temperature being regulated by a secondary air flap.

Attention is now being paid to the reduction in the dust content of the atmosphere of retort houses and other places where coke is handled. A. H. Cowan<sup>46</sup> has described dust extraction plant and has discussed the details of design and the methods of getting the dust into the extraction duct; and of subsequent handling.

### Gas plants in Germany

Early in the year it was announced<sup>47</sup> that all Ruhr gas plants are again working and are supplying gas to the grid, though much has yet to be done to remedy war damage. The Ruhr Gas Co. is again supplying gas as far east as Berlin, in the South beyond Frankfurt, and in the South-West of the Saar. West of the Rhine the lines are owned jointly with the Thyssen Gas and Water Works. The gas is purified for long-distance transmission and compressed at each of the 50 coke-oven plants which are linked to the grid. The gas for Frankfurt passes through an additional condensing station near Seigen. Repair teams are posted over the supply area. All points can inter-communicate by telephone to a central station at Essen and at this station there is a record of the gas pressure at all important coke-oven plants.

Particulars of the present position of the South Yorkshire gas grid have been published during the year.<sup>48</sup> The crude gas grid now comprises 72 miles of pipeline in various sizes from 8–24 in. diameter, 52 miles being above 12 in., and collects the gas from 12 coking plants which supply some 13,000 million cu. ft. of gas per year. Twelve gas undertakings have been absorbed into the Sheffield Gas Company which supplies very large quantities of gas to industry.

A scheme for another proposed gas supply system has been published for the western portion of South Wales, based primarily on the Margam coke ovens of the Steel Company of Wales. The needs of the district for gas are growing faster than new plant can be built. Margam steel-works are to use oil and this will liberate in 1951 some 22 million cu. ft. of gas per day.<sup>49</sup> The price proposed is 1s. 11½d. a 1000 cu. ft. at ovens. The proposed network will comprise 68 miles of main varying in size from 5–24 in. in diameter, about half being of 12 in. diameter or over. It is proposed to connect up 13 gas undertakings. The existing plants in these undertakings will cease making gas if the scheme is approved, and for a few years the supply will be entirely by coke-oven gas. If no more coke-oven gas is then available, as the demand grows it will be met by restarting the existing plant at the several works of the gas undertakings.

Home refining of petroleum has now become established and new refineries in this country are projected to treat about 20 million tons of crude oil a year.<sup>50</sup> This may have the effect of providing another source of gas. An arrangement has already been made between Manchester

Oil Refineries Ltd., and the Manchester Corporation Gas Department for the purchase by the Gas Department of considerable quantities of "tail" gases from the works of Petrochemicals Ltd., at Partington. The oil-refining process and the arrangements for gas supply have been described.<sup>51</sup>

### Purification and storage

The emphasis during this year seems to have been on oxide purification, possibly because the Gas Research Board has started an investigation into the causes of hardening of oxides during the purification of town gas from hydrogen sulphide. G. U. Hopton, Chairman of the Advisory Panel on Gas Purification of the Gas Research Board, has summarised existing knowledge and practice in oxidation purification<sup>52</sup> in the light of recent discoveries of the various forms of iron oxide and their behaviour under conditions met with in purifiers. An interim report from the Gas Research Board<sup>53</sup> has given the results of inquiries at gasworks and coke ovens in an endeavour to assess the reason for the hardening of oxide in purifiers. This does not occur in all purifiers; at some works it is chronic, while other works are free from it. It has been established that purifiers can be kept free from hardening troubles if suitable precautions are taken. There would seem to be several causes, the most important being the use of too dense oxide. The density should be below 25 lb./cu. ft. and this can be secured by careful packing, especially by not allowing the oxide to fall for a distance of more than 1-2 ft. when filling the boxes. Mechanisation and deep purifiers were noted as possibly contributing to the density of the oxide. Complete removal of tar fog is of great importance, and there is a hint that it may be found preferable to put the benzole plant in front of the purifiers to remove any polymerisable compounds contained in the gas. Tar cannot be removed wholly unless the gas is thoroughly cooled before being passed through electrostatic detarrers. The distribution of the deposited sulphur should be uniform over the volume of the oxide, this being secured by regular reversal of flow or, if this is impracticable, by removing the oxide from the boxes periodically and mixing it thoroughly before returning it. A high rate of gas flow, giving little time for polymerisation of compounds carried in the gas tends to prevent hardening. It is noted that at one works where no hardening difficulties occur, care is taken to charge the oxide at minimum density, to use two catch-boxes for each set of purifiers thereby allowing fouling to take place under conditions whereby the sulphur is distributed uniformly through the oxide, and to maintain a rapid stream of gas through the boxes.

Fluidisation technique has been applied to many industrial processes in America. R. H. Williamson and J. E. Garside<sup>54</sup> have described preliminary experiments and the proposed layout of a plant for the application of this process to oxide purification.

A new method of insulating purifiers has been indicated by R. L. Greaves,<sup>55</sup> in which glass fibre mats are attached to the purifier sides by thick red lead paint. Aluminium sheets, 18-gauge, with polished surfaces were used to give weather protection to the insulation. A gap of 2 in. was left between the sheets and the mats.

J. A. Spears has investigated the influence of packing density in purifiers on resistance to gas flow and has concluded that the optimum values of moisture to give the minimum resistance appears to be slightly greater than that to give the maximum voidage, due to increase in surface friction when the surface is completely covered with water. As, however, the water will evaporate when gas is passed through it for any considerable time, the maximum voidage should be the objective when filling boxes. L. Fassina<sup>57</sup> has given an account of the properties and performance of a new dry purification material consisting of iron and manganese hydrates, suitably mixed with sawdust.

The methods adopted for the treatment of crude coal gas prior to hydrogen sulphide removal at the Beckton coke-oven plant of the Gas Light & Coke Co. have been described by S. Pexton, D. Dougill, and L. A. Ravald.<sup>58</sup> The objective is to supply to the ammonia washers gas which is adequately cooled, freed from tar fog and from oily condensates and unsaturated with respect to naphthalene. In order to secure these objectives solid naphthalene deposits must not be allowed to accumulate on the cooling surfaces of the primary condensers. In accordance with this principle the gas on leaving the retort house passes in order through: (1) reversible primary water-cooled condensers, (2) exhauster, (3) first electrostatic precipitator to remove tar fog, (4) naphthalene washer, (5) non-reversible secondary water-cooled condenser, (6) second electrostatic precipitator to remove oil fog, (7) ammonia washers. Periodic reversal of gas and water flow through each condenser keeps surfaces free from naphthalene; but since normal reversals of flow are unlikely to remove naphthalene from the middle passes of the condenser, occasionally all three condensers remain for a time in the gas stream and the water flow is reduced to each in turn to raise its temperature sufficiently to remove naphthalene from this portion of the tubes. The temperature following the exhauster is 18°C. and the electrostatic precipitator is included at this stage to prevent the oil from the naphthalene washer from becoming contaminated with tar. Since gas oil used for naphthalene washing deteriorates in gas-making quality, the present practice of using the spent gas oil for carburetted water-gas manufacture has been replaced by a new process in which the naphthalene from the spent oil is removed by distillation in a unit provided for the purpose and passed back into the gas stream at the inlet of the primary condensers to be taken up in the tar. The gas, free from naphthalene, can then be passed into a non-reversible water-cooled secondary condenser. Cold water is supplied from forced draught water-cooling towers. The secondary electrostatic precipitator is included because oil from the naphthalene washer may condense to create an oil fog.

S. J. D. Williams<sup>59</sup> has recorded that "the most objectionable smell that emanates from a gasworks can be ascribed to the emptying and revivifying of spent oxide. . . . Many men at the present time flatly refuse to do this unpleasant work even at enhanced rates of pay." He emphasises the need for a reliable wet process which will work automatically and avoid these difficulties. This view is very generally held in the British gas industry.

The costs of the Manchester wet purification process have been given

by R. Walker.<sup>60,61</sup> The plant deals with 2 million cu. ft. of gas per day and it is stated that "no difficulty is experienced in maintaining gas free from  $H_2S$  to meet statutory obligations. . . . The capital cost of the liquid purification plant is only 60% of the dry box system and considerably less ground space is required. . . . Experience shows that a 75% crude sulphur can be produced which is more suitable for the manufacture of sulphuric acid than spent oxide and commands a price of £4 10s. per ton. On a large scale plant, commercially pure sulphur could be produced and a price of £8 9s. a ton obtained." The detailed costs for April 1948, during which just over 60 million cu. ft. of gas were purified are as follows :

	£	s.	d.
Attendant's wages . . . . .	49	15	2
Process materials :			
Copperas . . . . .	33	0	0
Soda ash . . . . .	6	14	5
Haulage on copperas and soda ash . . . . .	3	12	0
Electricity . . . . .	72	19	2
Steam . . . . .	74	3	10
Repairs and maintenance :			
Materials . . . . .	17	8	8
Wages . . . . .	17	8	2
Sundries . . . . .	10	7	2
<hr/>			
Total . . . . .	285	8	7
Less value of recovered sulphur . . . . .	73	19	0
<hr/>			
Net cost . . . . .	211	9	7
Gas purified (1,000 cu. ft.) . . . . .	60,087		
Cost per 1,000 cu. ft. . . . .			0.84d.

A description has been given of the Staatsmijnen-Otto process for removal of hydrogen sulphide from coal gas by washing with a suspension of Prussian blue in diluted ammonia.<sup>62</sup> The solution is regenerated in a separate aerator by passing compressed air through a column of the spent liquid whereby the hydrogen sulphide is oxidised to sulphur which floats on the solution as a froth, the blue acting as an oxygen carrier. Hydrogen cyanide is eliminated simultaneously forming ammonium thiocyanide. The sulphur as recovered contains about 70% of water, ammonium salts and blue, and after being filtered and washed is heated with water in an autoclave. The molten sulphur is drawn off, heated in an open vessel at 300° C. to decompose organic impurities, and distilled to produce pure sulphur. A comprehensive account of the various liquid purification processes proposed and in operation has been given by J. R. Marshall,<sup>63</sup> who concludes that tower purifiers and liquid purification processes will take the place of the normal oxide boxes.

An investigation upon the formation of oxides of nitrogen during the carbonisation of coal is reported by F. Magot-Cuvru<sup>64</sup> in which coal was carbonised at temperatures between 600° and 900° C. under conditions in which air was completely eliminated from the retort. It was established that oxides of nitrogen were formed only when there is re-entry of air and that the proportion produced increases with the temperature for the same volume of air ; the greater the volume of air introduced the greater is the volume of oxides of nitrogen produced. The formation of

oxides of nitrogen, therefore, arise only from incomplete combustion of nitrogen by oxygen and not from a reaction of air with ammoniacal products of the coal.

Stourbridge Corporation Gas Department for many years evaporated gas liquor on the furnaces and put the rest down the drains—until complaints caused them to put in a concentrated liquor plant. It is stated<sup>65</sup> that the plant is not profitable financially but is effective in relieving the undertaking from outside complaints.

Although at some plants in America concentrated ammonia liquor or various ammonium salts are produced and sometimes ammonia is deliberately destroyed, it is believed<sup>66</sup> that no process as yet seriously challenges the semi-direct sulphate process. The manufacture of sulphate of ammonia is still the best method of disposing of the ammonia produced at most coke-oven plants.

In 1944, R. H. Griffith and J. H. G. Plant<sup>67</sup> described work on a plant scale at Harrow gasworks for the catalytic removal of organic sulphur compounds from coal gas. The subsequent development of this process has been described by J. H. G. Plant and W. B. S. Newling.<sup>68</sup> This process may now be said to be ready for general use. The cost at Harrow in 1939 was 0.135d. a therm; since then prices have doubled or trebled but the process has been improved and the cost is now 0.189d. a therm. The process involves the catalytic transformation of organic sulphur (thiophene excepted, but this is removed during benzole recovery) into  $H_2S$ . The catalyst is nickel sub-sulphide,  $Ni_3S_2$ , operating at 360–400° C. The necessary temperature is provided by adding air to the gas, and passing the gas-air mixture into the catalyst bed, when part of the hydrogen in the gas is burned. The use of an efficient heat exchange (outgoing hot gas to incoming cold gas) enables the hot gas to be cooled to 80° C. and the cold gas to be heated to 300° C., with reduction in the consumption of hydrogen from the original figure of 2.5% to 1.6%. So long as the catalyst is kept above 350° C. it does not become seriously fouled by uncarbonised gummy polymers. A new form of catalyst chamber has been designed. The catalyst is regenerated from time to time by burning deposited carbonaceous matter in a current of air, the temperature being kept below 600–700° C.

A review of gas purification and by-product recovery was given by C. Cooper and D. M. Henshaw<sup>69</sup> to the Institution of Gas Engineers in the series of papers to which reference has previously been made. These authors believe that the semi-direct process of ammonia recovery is likely to prove the most economical in labour cost. The gas industry is not getting the best return from sulphur. Effluent disposal is likely to be a source of embarrassment in siting new works. The tower system of purifiers is indicated as removing some of the difficulties encountered with oxide boxes. Many liquid purification systems which have been adopted in America and elsewhere have not had to purify the gas to the statutory degree of purity required in Britain. The most serious deterrent to the use of liquid purification processes now is the risk of break-down: for this reason a very large manufacturing station with several streams of gas is likely to prove more suitable for liquid purification than smaller works. There is now experience over many years with the

Staatsmijnen-Otto process, and the Manchester process is under development. There are advantages in carrying out all gas purification under high pressures particularly when the gas is to be pumped some distance, as benzole recovery, organic sulphur removal, gas dehydration are all very much facilitated. The need for recovering benzole from all carbonising plants is considered to be as great as at any time, since benzole may well prove a valuable export.

The use of a purging machine for removing residual combustible gas from gasholder crowns and other gas plant is now well established. A modification of this practice was described by S. Jones<sup>70</sup> in which solid  $\text{CO}_2$  ("Drikold") was dropped into the water in a holder tank. The volume to be purged was 4500 cu. ft. and 5 cwt. of "Drikold" was dropped in through a manhole cover, an operation taking two minutes, after which a wooden plug was then removed from a 3 in. hole in the top of the crown, and manhole cover was replaced.  $\text{CO}_2$  was evolved rapidly for about an hour and gradually for another four hours. It was concluded that this method is simple, rapid and effective though it would apply only for small holders and tanks where the cost of hiring and transporting a purging machine would not be justified.

A new technique of cleaning metal (*e.g.*, gasholder) surfaces before repainting has been described by G. W. Rigby.<sup>71,72</sup> Brush-shaped oxy-acetylene flames, produced in a burner of special design are passed over the surface at a speed determined by the thickness of metal and state of corrosion. Unbonded mill-scale is removed by reason of differential expansion. Corrosion products in part come away similarly and in part are reduced to a powder which can be brushed off. Old paint comes away with the corrosion products or is burnt off. The warm, dry metal is wire-brushed and immediately painted.

### Benzole, tar and tar products

A new industrial research organisation, the Coal Tar Research Association, has been set up by the British Tar Confederation on the basis of a scheme originally proposed by the Association of Tar Distillers.<sup>73</sup>

A working party, operating under the Economic Commission for Europe, has reported that hardly 50% of Europe's pitch needs is being met and that the output of briquettes is correspondingly restricted.<sup>74</sup> Britain and the U.S.A. are the largest exporters of briquetting pitch to Europe, while France is the principal importer, receiving approximately 70% of all European imports; most of the remainder goes to Belgium and the Netherlands.

Coal-tar pitch, according to S. C. Ghosh and H. L. Riley,<sup>75</sup> contains a large proportion of substances which on carbonisation behave crystallographically in a manner similar to that of the bitumens present in coke and coal. The properties of the fractions obtained from the pitch by solvent extraction have been investigated both before and after air blowing. Although the air blowing brings about changes in the property of the pitch and fractions, no evidence is provided by the experiments of any appreciable oxidation and it is probable that the changes arise from polymerisation.

A paper, as yet unpublished, by G. Baars<sup>76</sup> on petroleum pipe still

practice has been made the basis of an important discussion on the design of pipe stills in general with special reference to the distillation of coal tar.<sup>77</sup>

The Road Research Laboratory of the D.S.I.R. and the British Road Tar Association are undertaking researches on the utilisation of road tar in collaboration with the Ministry of Transport. A report has been issued by the Road Tar Research Committee<sup>78</sup> on the adhesion of tar to aggregate. Adhesion is affected by the shape of the joint and by such properties of the adhesive as deformability, ductility, freedom from brittleness, elasticity and flexibility, particularly under rapidly applied loads. An adhesive joint may be weak because the liquid cannot dry between non-porous surfaces: resistance to water, time of set, length of useful life to be expected and cost are other important factors in the choice of an adhesive. The initial set of tar on a surface in practice is produced by the immediate increase in viscosity due to cooling (or to the breaking of an emulsion, when an emulsion is used). Subsequent loss of volatile constituents causes a further increase in viscosity and further strengthening of the adhesive bonds. Cubical chippings of uniform size spread to shoulder-to-shoulder cover give the best geometric joints. When water is present, low-aromatic tars give a better initial bond than do high-aromatic tars. Premature failures have been known to occur owing to rain water displacing tar from newly laid surfaces: here the chemical nature of the stone and tar affects the forces of attraction between them, but while low viscosity of the tar and smoothness of the stone permit these adhesive forces to take effect quickly, they also enable the tar to be displaced by water more readily. Methods are given for the measurement of adhesion between tar and stone. There is a general belief that the composition of the stone affects adhesion in that the geologically acid rocks give poor adhesion, while the basic rocks give good adhesion; laboratory experiments have failed to disclose any ground for this belief, and the physical, mechanical and geometric characteristics of the stones may in fact be the predominating factors. Addition of lime to the stone before coating with tar makes it possible to coat stone which is saturated with water.

The recovery from coal carbonisation of chemical intermediates lying within the field of benzole and tar products has been the subject of some interest during the year. The development of home refining of petroleum seems likely to give impetus to the production from petroleum of many chemicals that might otherwise have been manufactured from the by-products of coal carbonisation.<sup>77</sup> Among the new starting materials that might well have been studied earlier, is ethylene. The British Oxygen's process for the recovery of ethylene from coke oven gas has been described by P. M. Schuftan.<sup>79</sup> Gas, freed from tar, ammonia, naphthalene and benzene, but not from  $H_2S$  and  $HCN$  is compressed to about 20 lb./sq. in. and cooled to  $-135^\circ C.$  in two stages first in a regenerator and then with liquid methane in a heated chamber. Fractions of ethylene, ethane and methane respectively equivalent to 6, 3 and 1% of the thermal value of the inlet gas are separated, and the outlet gas returned to the coke oven for heating. The calorific value of the gas drops by about 70 B.Th.U./cu. ft. in the process. A pilot plant has been erected at Corby and is dealing with 350,000 cu. ft./hr. of coke-oven gas.

The annual output of ethylene (99% purity) is stated to be nearly 2000 tons or approximately 8 tons a 1000 tons of coal carbonised. The energy consumption is about 3700 kWh. per ton of ethylene.

New plant erected at the Kearny, N.J., Koppers Seaboard coke plant will be the first of its kind to recover pure liquid hydrogen cyanide as a marketable product.<sup>80</sup> HCN and H<sub>2</sub>S will be absorbed in an aqueous solution of soda ash, the solution heated under vacuum and the effluent gases passed through another water solution which absorbs the HCN. The residual sulphide will pass through the burners of a sulphuric acid unit.

Sludging and corrosion in benzole absorption plants has been a serious difficulty on some plants for many years. The Benzole Technical Committee of the Ministry of Fuel and Power investigated this subject during the war and has published its findings.<sup>81</sup> It is suggested that the sludging may be eliminated or diminished by operating the benzole-recovery plant wherever possible on purified gas, by precipitating the tar completely and at as low a temperature as possible (*e.g.*, 15° C.), by pre-scrubbing the gas with a small quantity of oil which is not again mixed with the wash oil, by reducing the amount of oxygen entering the oil in circulation to the minimum, by keeping the temperature of the oil during stripping below 130° C., and by other measures of lesser importance; the practical palliative is to use an oil regeneration plant to keep the wash oil in good condition, and to avoid accumulations of sludge in the benzole plant. Sludging was found to occur with all types of wash oil, the sludge is, however, much more soluble in creosote oil than in (petroleum) gas oil. It appears to be formed primarily from such bodies as indene by their oxidation to substances analogous to gums.

G. Cellan-Jones<sup>82</sup> has reported further progress with the "gas up-grading" process in which it is claimed that the benzole yield is improved by circulating through the free space above the charge in the coke oven during the last third of the carbonising period de-benzolised gas that has been through the by-product plant. In the application of this process to existing coke-oven batteries an increase in yield of about 14% is indicated by the working results described in this article.

## Gasification

### *Town gas*

Little of note appears to have been published during the year under review on the high-pressure gasification of coal for the production of gas of town gas quality. The Director of Research to the Gas Research Board has reported that with the experience now accumulated in this research, it is realised that the design of the original pressure vessel intended for the hydrogenation of coal under pressure imposes certain limitations upon the programme of experiments and accordingly consideration is being given to the practicability of obtaining a new vessel designed for the study of British coals in different atmospheres of steam and air, and ultimately of steam and oxygen.<sup>83</sup> One of the principal conclusions arising from the results obtained from the autogenous hydrogenation of fuel in a static bed is that the yield of methane obtained at

pressures such as 50 atmospheres is eventually limited by the exothermic reactions which cause the temperature to rise until further methane formation is rendered impossible through the establishment of equilibrium. As the result of this, interest has been aroused in British circles in the fluidisation technique developed in the oil industry and also in the German work on the gasification of powdered coal (to be discussed later under "Producer Gas").

The use of oxygen in town gas manufacture was discussed by F. J. Dent<sup>84</sup> in a paper (as yet unpublished) to a joint conference of the Institution of Chemical Engineers and the Physical Society. Oxygen is used in the Lurgi process, which is the prototype of the Gas Research Board process, by which continuous gasification under pressure enables a gas of high C.V. to be obtained without dilution by nitrogen and by the production of some 20% or so of methane through working at higher pressures. The gas is produced at high pressure and is thus suitable for long-distance transmission without further compression.<sup>85</sup> German plants use low-priced fuels such as lignite and do not recover waste heat, so that although the generator efficiency may be 74%, the overall efficiency may be only 50%. Dent calculates that the thermal efficiency of the pressure gasification process using oxygen compares favourably with that of other total gasification processes used or proposed for use in the gas industry :

System	C.V. of gas B.Th.U./cu. ft.	Estimated overall thermal efficiency %
Carbonisation :		
B.W.G.—no enrichment .. .. .	350	60
B.W.G.—catalytic synthesis .. .. .	450	59
	500	58
Pressure gasification of coke—catalytic synthesis	450	61
	500	60
Pressure gasification of coal using oxygen .. .. .	about 450	72

Loss of thermal efficiency due to the power required for oxygen production should not be regarded as a decisive factor in considering high-pressure gasification for a large base-load station. The cost of a gas-making plant would be much the same as for the carbonisation systems now in use. The advantage of low capital expenditure normally found with gasification plant is likely to be counterbalanced partly by the incorporation of the oxygen plant and partly by the increased costs of construction due to the high operating pressure. J. H. Rushton and G. R. Downs<sup>85</sup> maintain that the high capital cost of oxygen plant renders its discontinuous use uneconomic and that gasification processes depending on oxygen are therefore only suitable for making base-load gas.

### Producer-gas

A good deal of interest has been aroused in processes of gasification in a stream of powdered solid fuel. Koelbel, chemist in charge of the Rheinpreussen plant, has expressed the view that the most promising development of gasification is the Koppers continuous producer in which pulverised brown coal, anthracite duff, or washery slurry is transported

by a stream of oxygen into a refractory-lined combustion chamber into which superheated steam is blown.<sup>86</sup> (The Koppers process was described in F.I.A.T. Final Report 1303.) Similarly, the view has been expressed<sup>87</sup> that U.S. requirements for synthesis gas will probably best be met by the pulverised fuel suspension (*e.g.*, Koppers) type of process on the ground that it can be applied to the widest range of coals, subject to reasonably good grinding characteristics, and because the gas is relatively free from hydrocarbons and organic sulphur compounds.

The thermal efficiency of gas producers has been discussed by A. C. Dunningham.<sup>88</sup> Defining "thermal efficiency" as the percentage of input heat recovered in the gas, he notes that a hot gas efficiency can be determined from the difference between heat input and heat losses. These losses are (a) heat in carbon in ashes and dust, which should not exceed 2%, (b) radiation and unaccounted-for losses, which should not exceed 6%, and (c) losses in undecomposed steam. This last he determines from the expression

$$P = \frac{a - x}{z + y} \times 100$$

where P = percentage of undecomposed water vapour in gas, *a* = total water vapour in gas, *x* = free and inherent water in fuel, *z* = water vapour present in blast, and *y* = total hydrogen in fuel expressed as water. The relationship between blast saturation and temperature, and heat losses has been determined from examination of many published results as follows :

Blast saturation temperature—°C. . . . .	60	55	60	65	70
Percentage decomposition of water vapour . . . . .	83	80	76	72	66
Percentage undecomposed steam . . . . .	17	20	24	28	34
Percent heat losses arising from undecomposed steam, excluding water in fuel . . . . .	1.5	2.1	2.8	3.7	5.1
Losses as :					
Radiation and convection ( <i>v. ante</i> ) . . . . .	6	6	6	6	6
Carbon in ashes and dust ( <i>v. ante</i> ) . . . . .	2	2	2	2	2
Heat in undecomposed steam (as above) . . . . .	1.5	2.1	2.8	3.7	5.1
Total losses . . . . .	9.5	10.1	10.8	11.7	13.1
"Bogey" gross hot-gas efficiency (by diff.) . . . . .	90.5	89.9	89.2	88.3	86.9

Net hot-gas efficiencies are obtained by deducting from the gross figures the heat in water vapour formed by combustion of hydrogen in the gas (typically 5% for coal and anthracite and 3% for coke); thus "bogey" hot-gas efficiency at 55° C. B.S.T. for bituminous coal and anthracite is 84.9% and for coke is 86.9%. Cold-gas efficiencies require deduction from these figures of the heat lost in cooling the gas, *i.e.*, its sensible heat and the heat of combustion of tar and soot removed during cleaning. Hot-gas efficiencies in all producers, whether fired with coal, coke or anthracite, should not be less than 85% on this basis. Cold-gas efficiencies are lowest with bituminous coal owing to tar formation. Sensible heat should be recovered where possible, but expensive producer fuel should not be used for the production of steam so that water-jackets and waste heat boilers should be avoided wherever possible in favour of recuperators

or preheating the air blast. According to the fuel used, the cost of a therm of hot producer-gas varies from 1.5 to 2.0 times that of a therm of bituminous coal, whilst for cold-gas the ratio is similarly from 2.0 to 2.5. These ratios represent not only the relative costs of a therm as delivered to the furnace but also on an available therm when the coal is fired on mechanical stokers, and in such cases overall capital and operating costs are likely to be similar.

### Water-gas

J. F. Foster<sup>89</sup> reports an experimental investigation into a continuous process for manufacturing water-gas in which pulverised coal and steam flow together down an externally heated tube. It is concluded that the capital cost of a plant to put such a process into operation would be so much higher than that of a conventional process as to preclude commercial application.

The twin generator oil-gas process now in operation at Buffalo, U.S.A., has been described by G. S. Knight to the Canadian Gas Association.<sup>90</sup> A standard 3-shell water-gas set was modified structurally to permit of the use of oil in place of solid fuel in the regenerator. This involved changing the connections, and the automatic control arrangements and adding chequer brick in the generator. During the first part of the cycle the heating oil and air are admitted simultaneously to generators No. 1 and No. 2, No. 2 being the former carburettor. This oil in burning heats the chequers in all three shells and the waste products pass to atmosphere through the stack valve at the top of the superheater. The blow part of the cycle continues until a temperature of 870° c. is reached at the top of the superheater chequers, at which time the air and heating oil are shut off and the make oil and make steam turned on. The stack valve is closed and the make gases pass through the wash box and relief holder. It is expected that when certain further modifications have been made the set will make 400,000 cu. ft. of gas of 900 B.Th.U./cu. ft. of a specific gravity of 0.82. The oil used is No. 1 or No. 3 and it is stated that the oil consumed in U.S. gal./1000 cu. ft. is 1.5 gallon for heating and 9.5 gallon for gas-making. The cycle is of 4 minutes duration and the set can be operated by one man. Claims made are the elimination of fire cleaning and charging; continuous, uniform, 24 hr. operation; cracking of oil in a controlled steam atmosphere; increased output for the capital invested.

### Underground gasification

Underground gasification is stated to have been proved possible in Russia but few results have been published.<sup>91</sup> It is understood that the stream method is favoured in the Donetz basin and that the C.V. of the gas ordinarily obtained is 100-110 B.Th.U./cu. ft., though higher values are possible by the use of air enriched with oxygen or steam. In Belgium, estimates collected on the basis of experiments in that country have led to the conclusion by P. Demart that underground gasification is more economical than existing mining methods. The tests on underground gasification of coal carried out by the Société Co-operative de Gaziëfication Soutersinc, near Liège, Belgium, especially experiments made in

February and March 1948 are said to be so encouraging that further experiments are to be undertaken which are expected to lead to important progress in the development of this technique.<sup>92</sup> In consequence, Charbonnages de France, the administration of the French coal industry, has decided to support the project technically and financially.

The Gas Research Board<sup>93</sup> has surveyed the literature on the underground gasification of coal and has published a bibliography up to the end of the year 1944.

### Price structure of fuels

The price structure of solid fuels has been a contentious problem for many years. If fuels are to be used to the best purpose, there must be a price structure which expresses their relative value, and the structure must be stable so that users may be assured that when they install plant for burning a particular type of fuel, its price will continue to bear the same relation to those of other fuels.

E. S. Grumell<sup>94</sup> has published a comprehensive technical paper on the subject in which he considers that the price structure of coal should be based on three factors: (a) the number of heat units in the coal, (b) the efficiency with which those heat units can be used, taking into account the effect of moisture, ash, etc., and (c) a utility or convenience factor, covering capital and maintenance costs, and taking into account special features of the coal or of the manner in which it is used (*e.g.*, gas and by-product yields from coals used for carbonisation). Grumell's proposals may be summarised as follows: (1) the pithead price of every coal is to be determined on a standard coal of 280 therms a ton, and to be in direct proportion to the relative C.V., (2) to allow for variation in moisture content, deduct or add 0.45d. a ton for each 1% (or fraction) respectively above or below 7%, (3) deduct 1.57d. a ton for each 1% (or fraction) above 8%, (4) add 19d. a ton for graded coal, (5) to take account of the uniformity factor various additions to the price for "uniform" coals are proposed, without stating by what method "uniformity" is to be ascertained—nor in fact is it known what is the practical effect of uniformity, or the lack of it, (6) no allowance is made for the convenience or utility factor as this must await further information. These proposals have been subjected to detailed criticism from the point of view of their application to the carbonising industry.<sup>95</sup>

The National Coal Board is engaged in working out a price structure which shall properly assess the value of grades of solid fuel on technical and economic grounds. This is a matter of very great importance to all those engaged in the industries considered in this review. The Solid Smokeless Fuels Federation, too, has set up a Price Structure Committee<sup>96</sup> to consider amongst other things the relative value to the consumer of the various solid smokeless fuels (*e.g.*, oven coke, gas coke, Welsh steam coal, and anthracite) based on the calorific value, working efficiency, and the convenience factor, and to explore the development of a national price structure for solid smokeless fuel.

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# INTERMEDIATES AND COLOURING MATTERS

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COMPARED with the war years, the year under review has seen a considerable increase in the number of patent applications both for organic intermediates in general and, particularly, for dyestuffs. On the other hand, the number of reports covering the German chemical industry has fallen considerably and the only report of importance is F.I.A.T. 1313 (3 vols.) covering the manufacture of most of the intermediates and dyestuffs and items of research not fully covered in earlier reports (see bibliography to last year's review).

Output and trade statistics for the dyestuffs industry are again available and these are in line with the increased volume of patent applications. The total output from the main dyestuff-producing countries in 1947 was of the same order as the pre-war output—viz., 200,000–220,000 tons; France, Switzerland, the United States and Great Britain showed increases, whilst Germany, Italy, Japan and the U.S.S.R. showed decreases. Exports from Switzerland (9000 tons), United States (30,500 tons), and Great Britain (11,500 tons) were considerably larger in 1947 than in 1937, the most pronounced being shown by the United States (approximately 4 times judged by weight and 16 times judged by value). The United States output for 1947 has been given as 212 million lbs., of which 78 million were azo-dyes. This is rather more than 3 times the estimated output in Great Britain.

Although the output in Germany in 1947 was but a small fraction of the pre-war output, the total bomb damage to the main dyestuffs factories is sufficiently small that her potential production, given adequate man-power, fuel, etc., cannot be much below the pre-war figure.

## INTERMEDIATES (D. A. W. Adams, B.Sc., Ph.D.)

It is yearly becoming more difficult to review adequately progress in the manufacture of intermediates; the field of organic intermediates is now so vast that, to be comprehensible, a review must be confined to restricted topics. For the present purpose, therefore, a more limited definition of intermediates than that usually given is proposed, and attention will be confined to organic chemicals of general interest and to those specifically used in the manufacture of dyestuffs. Such fields as petroleum cracking (and the products derived therefrom), polymerisation, and pharmaceuticals (including their specific intermediates) are excluded as they are well covered in other sections of these reports. For certain topics, excluded last year for reasons of space, the review covers two years.

An excellent review has appeared recently<sup>1</sup> of developments during the last ten years in the general chemical reactions employed in the production of organic chemicals; of particular interest to readers of this section are the papers covering reduction,<sup>2</sup> ammonolysis,<sup>3</sup> halogenation,<sup>4</sup> hydration and hydrolysis,<sup>5</sup> nitration,<sup>6</sup> and sulphonation.<sup>7</sup>

### Aliphatic intermediates

Much of the published information on aliphatic compounds has concerned petroleum products and polymerisable compounds. Halogenated intermediates and aliphatic nitro-compounds are still receiving considerable attention, although the latter and fluoro-compounds are not the subject of so many patents as in the last few years. The manufacture of fluorinated compounds has been started in this country by Imperial Chemical Industries Ltd.<sup>8</sup> In all branches of aliphatic chemistry, particular attention is being paid to catalytic vapour-phase, continuous processes.

#### *Chlorinated hydrocarbons*

The Socony-Vacuum Oil Co., Inc., chlorinate methane and ethane, to form methyl chloride and ethyl chloride, by passing the vapour either at 400–525° through a finely divided porous carrier ( $\text{Al}_2\text{O}_3$ -gel) impregnated with  $\text{CuCl}_2$  and, preferably,  $\text{KCl}$ ,<sup>9</sup> or at 325–500° through molten  $\text{CuCl}_2$ - $\text{KCl}$  (60 : 40 mol.-%)<sup>10</sup>; in both processes the  $\text{CuCl}_2$  acts as chlorinating agent by reduction to  $\text{Cu}_2\text{Cl}_2$  and is regenerated in a second reactor by treatment at 325–425° (250–475° for the melt) either simultaneously or successively with air and  $\text{HCl}$  (recovered from the chlorination stage). In the case of  $\text{C}_2\text{H}_6$ , the reaction mixture contains 50.1 wt.-% of  $\text{EtCl}$  and 31.5 wt.-% of  $\text{C}_2\text{H}_4\text{Cl}_2$ . Alkyl chlorides, such as *sec.*-butyl and isopropyl chlorides, are made by Distillers Co.<sup>11</sup> by passing  $\text{HCl}$  into the dialkyl or alkyl hydrogen sulphates in 80–90%  $\text{H}_2\text{SO}_4$  at 15–60°; the spent acid is re-used for making the sulphates by adsorption of the olefines.

Methylene chloride is chlorinated continuously at 580–600° in presence of carbon deposited on glass-beads, with a contact time of 1.9 sec., to give a mixture containing  $\text{C}_2\text{Cl}_4$  (33.8),  $\text{CCl}_4$  (17.5),  $\text{C}_2\text{Cl}_6$  (14.5), and hexachlorobenzene (32.5%).<sup>12</sup> Dow Chemical Co.<sup>13</sup> obtain  $\text{C}_2\text{Cl}_4$  from  $\text{CH}_4$ ,  $\text{Cl}_2$  and  $\text{CCl}_4$  at  $> 500^\circ$ , whilst the same firm<sup>14</sup> chlorinate propane in presence of  $\text{CCl}_4$  or  $\text{C}_2\text{Cl}_4$  at 500–700° to obtain both diluents as the main products. Ethylene dichloride is obtained by A. A. F. Maxwell<sup>15</sup> by chlorination of  $\text{C}_2\text{H}_4$  in presence of a catalyst comprising  $\text{Pb}$  63%,  $\text{Ag}$  16%, and  $\text{Sb}$  21% on asbestos.

A variety of products can be obtained from acetylene depending on the chlorination conditions employed. Thus, interaction of  $\text{C}_2\text{H}_2$  with  $\text{Cl}_2$  and  $\text{HCl}$  at  $> 20^\circ$  in presence of actinic light, preferably in solution in the reaction product, gives  $\text{CH}_2\text{Cl-CHCl}_2$ <sup>16</sup>; absence of oxygen and the use of a low temperature reduce the formation of  $\text{C}_2\text{H}_2\text{Cl}_4$ . Hooker Electrochemical Co.,<sup>17</sup> however, pass  $\text{C}_2\text{H}_2$  and  $\text{Cl}_2$  into  $\text{C}_2\text{H}_2\text{Cl}_4$  at 70–95° in presence of comminuted iron (converted *in situ* into  $\text{FeCl}_3$ ) to obtain the diluent as main product. Monsanto Chemical Co.<sup>18</sup> treat  $\text{C}_2\text{H}_2$  with  $\text{HCl}$  in the vapour-phase in presence of a solid catalyst comprising

$\text{HgCl}_2\text{-CeCl}_2$  as a complex salt supported on charcoal and preferably in presence of a little free halogen to obtain vinyl chloride. When  $\text{C}_2\text{H}_2$  is passed through a solution of  $\text{CuCl}_2$  and  $\text{HgCl}_2$  in hydrochloric acid, however, *trans*-1 : 2-dichloroethylene is produced.<sup>19</sup>

Ethylene and hydrochloric acid are caused to react in a diluent (a hydrocarbon or chlorinated hydrocarbon), containing a suspension of carbon and  $\text{HgCl}_2$ , at 120–150°, to give vinyl chloride.<sup>20</sup> Approximately theoretical yields of  $\text{C}_2\text{Cl}_6$  are obtained by chlorinating  $\text{C}_2\text{Cl}_4$  either at 49°/74 lb. per sq.in.<sup>21</sup> or at 60° under reflux in presence of actinic light.<sup>22</sup>

An account of the manufacture of allyl chloride by chlorination of  $\text{C}_3\text{H}_6$  at 550–570° and of its hydrolysis to allyl alcohol has been given by Fairbairn, Cheney, and Cherniavsky.<sup>23</sup> Chlorination of butadiene at 65–75° gives a mixture of 1 : 4-dichlorobut-2-ene and 3 : 4-dichlorobut-1-ene,<sup>24</sup> but when octachloropenta-1 : 3-diene is chlorinated at 130° the molecule is split giving  $\text{C}_2\text{Cl}_6$  and  $\text{CCl}_4$ .<sup>25</sup> 1 : 4-Dihalogenobut-2-yne are made by Imperial Chemical Industries Ltd. by treating  $(\text{C}\cdot\text{CH}_2\text{OH})_2$  with a halide or oxyhalide of S or P in pyridine or benzene.<sup>26</sup>

Chlorination of methyl cyanide with chlorine or sulphuryl chloride at 320–440° in presence of pumice containing  $\text{AgCl}$  gives  $\text{CCl}_3\text{CN}$  in 62–85% yield.<sup>27</sup> The halogenated vinyl cyanides have been claimed by Dow Chemical Co. as insecticides.<sup>28</sup>

#### *Aliphatic fluoro-compounds*

Modifications of the standard procedures for replacing chlorine by fluorine in chlorinated hydrocarbons continue to be claimed. Thus Phillips Petroleum Co. use hydrofluoric acid in presence of  $\text{TiF}_4$  for converting  $\text{CCl}_4$  into  $\text{CCl}_2\text{F}_2$ .<sup>29</sup> E. I. Du Pont de Nemours & Co.<sup>30</sup> heat chlorinated butanes with  $\text{HF}$  in presence of  $\text{HgO}$  or with antimony fluoride to replace one or two chlorines by fluorine; thus,  $\text{CMeCl}_2\cdot\text{CHMeCl}$  gives either 2 : 3-dichloro-2-fluoro-*n*-butane or 3-chloro-2 : 2-difluoro-*n*-butane according to the conditions used. Imperial Chemical Industries Ltd.<sup>31</sup> replace chlorine in compounds having 3 halogens attached to the same C atom by heating with  $\text{HF}$  in presence of a complex of  $\text{HF}$  and an antimony pentahalide containing at least 3 fluorine atoms. In this way,  $\text{CHF}_3$  is obtained in 100% yield from  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}\cdot\text{CF}_3$  in 90–95% yield from  $\text{CH}_2\text{Cl}\cdot\text{CClF}_2$ .

Imperial Chemical Industries Ltd.<sup>32</sup> obtain alkenyl fluorides by passing a mixture of an alkyne of mol.wt. < 85 and  $\text{HF}$  at 30–100° over a catalyst containing a mercuric salt such as  $\text{Hg}(\text{OAc})_2$ ,  $\text{HgCl}\cdot\text{NH}_2$ ,  $\text{HgCl}\cdot\text{CH} : \text{CHCl}$ , etc.;  $\text{CH}_2 : \text{CHF}$  and  $\text{CH}_2 : \text{CH}\cdot\text{CF} : \text{CH}_2$  are obtained from  $\text{C}_2\text{H}_2$  and  $\text{CH}_2 : \text{CH}\cdot\text{C} : \text{CH}$ , respectively.

Ethylene tetrafluoride is very reactive and E. I. Du Pont de Nemours & Co. have found that it condenses readily with a variety of organic compounds. Thus,  $\text{CH}_2 : \text{CH}\cdot\text{CN}$  gives 2 : 2 : 3 : 3-tetrafluoro-1-cyanocyclobutane, which can be hydrolysed to the carboxylic acid and to the amide,<sup>33</sup> whilst at 20–150°, iodine gives  $\text{ClF}_2\cdot\text{ClF}_2$ .<sup>34</sup>

Fluoroprene is obtained by addition of hydrogen fluoride to vinylacetylene by E. I. Du Pont de Nemours & Co.,<sup>35,36,37</sup> one process<sup>37</sup> using mercuric salts as catalyst.

American Viscose Corp.<sup>38</sup> treat polyfluoro-vinyl cyanides with ethanol at room temperature to obtain fluorocyanodiethyl ethers. Thus:  $\text{CF}_2\text{CCl}\cdot\text{CN}$  gives  $\text{OEt}\cdot\text{CF}_2\cdot\text{CHCl}\cdot\text{CN}$ , and  $\text{CF}_2\cdot\text{CF}\cdot\text{CN}$  gives  $\text{OEt}\cdot\text{CF}_2\cdot\text{CHF}\cdot\text{CN}$ .

Trifluoroacetic acid has been obtained by E. I. Du Pont de Nemours & Co.<sup>39</sup> by hydrolysis of  $\text{CCl}_3\cdot\text{CF}_3$  using a mixture of  $\text{HgSO}_4$ ,  $\text{Hg}_2\text{SO}_4$ , and oleum. Oxidation of 1:2-dichlorohexafluorocyclopentene gives hexafluoroglutamic acid,<sup>40</sup> whilst tetrafluorosuccinic acid is obtained similarly from 1:2-dichlorotetrafluorocyclobutene or hexafluorocyclobutene.<sup>41</sup> The preparation of difluoromalic acid from 3:3-difluoropenta-1:3-diene has also been described.<sup>42</sup>

Ethylfluorosulphonate is obtained by Universal Oil Products Co.<sup>43</sup> by interaction of  $\text{EtF}$  and  $\text{FSO}_3\text{H}$  at  $0^\circ$ .

Trifluoroethanol is obtained by Gilman and Jones<sup>44</sup> by hydrogenation of trifluoroacetamide using a platinum oxide catalyst, whilst Henne *et al.*<sup>45</sup> reduce ethyl trifluoroacetate with lithium aluminium hydride.

#### *Nitro-hydrocarbons, -alcohols, etc.*

The nitration of aliphatic compounds continues to receive attention although there appears to be less commercial interest in these compounds than appeared likely a year or two ago when there was considerable publication on this subject.

A review of the vapour-phase nitration of hydrocarbons has been given by Hass and Schechter.<sup>46</sup>

Vapour-phase nitration of paraffins, *e.g.*, propane, is carried out by Imperial Chemical Industries Ltd. in a converter having a tubular lining of vitreous or refractory material in absence of iron.<sup>47</sup>

Nitroso-nitrohydrocarbons and nitroalkyl nitrites are converted by the same firm<sup>48</sup> into dinitro-compounds or into nitroalkyl nitrates by treatment with  $\text{N}_2\text{O}_4$  or  $\text{NO}$  and  $\text{O}_2$  at  $0-20^\circ$ ;  $\text{NO}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO}_2$  is thus converted into  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO}_2$ . The same firm<sup>49</sup> obtain mixtures of dinitroalkanes and nitroalkanols by interaction of olefines or *cycloolefines* with  $\text{N}_2\text{O}_4$  (and  $\text{O}_2$ ); thus, *cyclohexene* gives 1:2-dinitrocyclohexane and 1-nitrocyclohexan-2-ol. Condensation of primary nitroparaffins and nitro-alcohols in a primary or *sec.* base (piperidine) gives dinitroalkanes.<sup>50</sup>

Dinitroparaffins or nitroalkyl nitrites having the two  $\text{NO}_2$  groups or the  $\text{NO}$  and  $\text{NO}_2$  on adjacent C atoms are converted by Imperial Chemical Industries Ltd. into nitroolefins by treating with a base at  $0^{51,52}$ ; when ammonia is used, ammonium nitrite is recovered. The same firm convert nitro-alcohols into nitro-olefines by heating with phthalic anhydride.<sup>53</sup> Visking Corp. obtain similar compounds by heating an ester of a nitro-alcohol at  $200-500^\circ$  in presence of an alkaline earth salt of a mineral acid.<sup>54</sup>

By interaction of nitroalkanes with unsaturated cyanides in presence of caustic soda, Imperial Chemical Industries Ltd. obtain nitroalkyl cyanides.<sup>55</sup> Thus nitroethane and vinyl cyanide give 3-nitrobutyl cyanide.

#### *Alcohols and ethers*

Procter and Gamble<sup>56,57,58</sup> have a number of patents covering the reduction of heavy metal salts of fatty acids to produce alcohols or esters depending on the metal salt employed. There are evidently difficulties in operating these processes and several different types of reactor are

favoured by different firms; E. I. Du Pont de Nemours & Co.,<sup>59,60</sup> for instance, employ a long tubular reactor having a ratio of length to width of  $\leq 50:1$ .

Imperial Chemical Industries Ltd.<sup>61</sup> prepare alcohols by hydrogenating furan or an alkylfuran at 200–300°/200 atm. under slightly acid conditions and in presence of a catalyst comprising a chromate of silver or copper. Furan itself gives *n*-butanol whilst 2-methylfuran gives a mixture of pentan-1-ol and pentan-2-ol.

C. Weizmann<sup>62</sup> uses a solvent of the type of  $\text{OEt} \cdot [\text{CH}_2]_2 \cdot \text{OBU}$  in the interaction of acetylenic hydrocarbons with aldehydes and ketones to give *sec.*- and *tert.*-ethynylcarbinols, whilst J. Zeltner and M. Gemas<sup>63</sup> prefer an acetal such as  $\text{CH}_2(\text{OMe})_2$ . Shell Development Co.<sup>64</sup> prepare similar alcohols by treating dihalogenated olefines with an aqueous solution of an alkali or alkaline earth hydroxide under such conditions that the product is removed as formed.

In the condensation of aldehydes or ketones ( $\text{COMe}_2$ ) with trihalogenomethanes ( $\text{CHCl}_3$ ) to give trihalogenated alcohols ( $\text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{OH}$ ), improved yields are claimed by E. Bergmann and M. Sulzbacher<sup>65</sup> by using as condensing agent a complex of KOH and a dialkyl ether of an aliphatic acetal or ketal such as  $\text{CH}_2(\text{OMe})_2$ .

Imperial Chemical Industries Ltd.<sup>66</sup> make vinyl ethers by interaction of acetylene at 150–250° with an alcohol and alkali alkoxide in a *sec.*- or *tert.*-aromatic amine as solvent.

#### Acids and esters

The electrolytic oxidation of ethanol to acetic acid in 3.2%  $\text{H}_2\text{SO}_4$  at platinum-gauze anodes has been studied by G. Zeller<sup>67</sup>; the formation of acetic acid varies during the operating period, being relatively low at first, then rising, and finally falling. Eastman Kodak Co.<sup>68</sup> oxidise mixtures of lower aliphatic alcohols ( $\text{EtOH}$ ) and aldehydes ( $\text{MeCHO}$ ) to acids ( $\text{AcOH}$ ) by passage with air through a tube containing a catalyst such as Ce, Nd, Ag, Hg, Pb, Th, Bi, or V acetate dissolved in acetic acid.

Imperial Chemical Industries Ltd.<sup>69</sup> hydrolyse compounds containing  $\cdot\text{CH} \cdot \text{CCl}_3$  or  $:\text{CCl}_2$  groups with 85–99%  $\text{H}_2\text{SO}_4$  to obtain carboxylic acids; for instance, 4-chlorobutane-1-carboxylic acid can be obtained from 1:1:1:5-tetrachloropentane or 1:1:1:5-trichloropent-1-ene. The Pennsylvania Salt Manufacturing Co.<sup>70</sup> oxidise trichloroaldehydes such as chloral to trichlorocarboxylic acids with  $\text{Ca}(\text{OCl})_2$  in aqueous solution at 50–100° and in presence of sufficient  $\text{CaCO}_3$  or  $\text{CaCl}_2$  to give  $p_H$  2–7. Halogenoacetyl halides ( $\text{CH}_2\text{Cl} \cdot \text{COCl}$ ) are prepared by E. I. Du Pont de Nemours & Co.<sup>71</sup> by interaction of a polyhalogenomethane with carbon monoxide at 100–250° in presence of a Friedel-Crafts catalyst.

Acrylic acid is obtained by Imperial Chemical Industries Ltd.<sup>72</sup> by treating  $\text{CH}_2$ :  $\text{CCl}_2$  and formaldehyde with 65–70% sulphuric acid at 30–60°. Crotonaldehyde is oxidised by C. Weizmann and M. Salzbacher<sup>73</sup> to the acid by liquid-phase air oxidation at 20–35° in presence of a catalyst comprising a mixture of the oleates of Pb (30.2), Mn (34.7) and Co (28.1%). Distillers Co.<sup>74</sup> claim higher yields in the same oxidation (with or without catalysts) by operating the process continuously.

E. I. Du Pont de Nemours & Co.<sup>75</sup> claim improved yields of adipic

acid from *cyclohexane* by oxidising firstly with air at  $145^{\circ}/100$  lb. per sq. in. and then treating the mixture containing *cyclohexanol* and *cyclohexanone* with nitric acid under pressure and in presence of  $\text{NH}_4\text{VO}_3$  and copper.

Dibasic acids are obtained by E. Lilly & Co.<sup>76</sup> by interaction of an acid (or anhydride, acid chloride, etc.) with  $\text{Ac}_2\text{O}_2$  at  $85\text{--}95^{\circ}$ ; *isobutyric* acid thus gives  $(\text{CMe}_2\cdot\text{CO}_2\text{H})_2$ . Resinous Products & Chemicals Co.<sup>77</sup> make 3-acetyl-3-alkylpentane-1:5-dicarboxylic acids by hydrolysis of the dicyanide obtained by condensing 2 mols. of vinyl cyanide with the appropriate methyl alkyl ketone; the use of an aldehyde in place of a ketone give aldehydocarboxylic acids.<sup>78</sup> Keto acids containing 8-12 C atoms are halogenated by National Oil Products<sup>79</sup> to give dihalogeno derivatives having the halogens on the C atoms adjacent to the keto group.

Carbide and Carbon Chemicals Corp.<sup>80</sup> prepare 1-cyanovinyl acetate and 1:1-dicyanoethyl acetate by treating keten (2-3 mols.) with anhydrous hydrocyanic acid (1 mol.) at  $-50^{\circ}$  in presence of a *tert.* amine, an alkoxide, etc., and in a solvent such as acetic anhydride. Esters of other cyanoalkane carboxylic acids are made by Mallinckrodt Chemical Works<sup>81</sup> by interaction of organic cyanides with an excess of a dialkyl carbonate under reflux and in presence of an alkali hydroxide.

Acetoacetic esters (e.g., ethyl acetoacetate) are prepared by Distillers Co.<sup>82</sup> by passing an alkyl 2-hydroxyalkane-1-carboxylate (e.g.,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ) over a dehydrogenating catalyst (Cu, Ag, or brass) at  $270\text{--}370^{\circ}$  preferably in presence of an inert gas and an unsaturated organic H-acceptor.

### *Aldehydes and ketones*

Modifications continue to be patented in the oxidation of methanol to formaldehyde. E. I. Du Pont de Nemours & Co. use a molybdenum or tungsten oxide catalyst promoted with vanadium or iron oxides.<sup>83</sup> The same firm also claim a mixture of a molybdenum oxide or molybdate and one or more metals chosen from Mn, Mg, Cd, Sr and Ba, promoted by a phosphate or sulphate<sup>84</sup>; alternatively, the molybdenum is used as promoter for a catalyst comprising a phosphate and one of the above metals.<sup>85</sup>

Good yields (14-20%) of metaldehyde are obtained by Publicker Industries Inc.<sup>86</sup> by polymerising  $\text{MeCHO}$  at  $0^{\circ}$  to  $-20^{\circ}$  in presence of 7-15% of an ether ( $\text{Et}_2\text{O}$  or dioxan) and a catalyst such as pyridine hydrobromide.

Aldol also continues to receive attention and continuous processes are claimed by both Air Reduction Co.<sup>87</sup> and S. A. Muller and A. R. Hammond.<sup>88</sup>

The acetone synthesis from acetylene and steam in presence of a  $\text{Fe}_2\text{O}_3\text{--ZnO}$  catalyst as developed by Shawinigan Chemicals has been described.<sup>89</sup> Distillers Co.<sup>90</sup> make methyl ethyl ketone by a continuous process in which butane-2:3-diol is added to a mixture containing 5-10 wt.-% of a strong acid. Universal Oil Products<sup>91</sup> obtain *isopropyl isobutyl* ketone [2:5-dimethylhexan-3-one], together with some *isobutyl* butyrate by interaction of propane and carbon monoxide in presence of  $\text{AlCl}_3$  and  $\text{HCl}$  at  $80^{\circ}/125$  atmospheres.

Chloral is still attracting considerable attention because of its importance in the preparation of DDT. E. I. Du Pont de Nemours & Co.<sup>92</sup> describe its manufacture by a two-stage process, chlorination being effected firstly at 50–60° and finally at 80–90°; depending on whether 95 or 70%  $\text{H}_2\text{SO}_4$  is used the intermediate product is either mainly  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OEt}$  or  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ . Imperial Chemical Industries Ltd.<sup>93</sup> decompose the chloral alcoholate by continuously adding it to  $\text{H}_2\text{SO}_4$  (maintained at 60–80% strength) at 110–160° so that the chloral distils off continuously.

Unsaturated aldehydes containing  $> 7$  C atoms are prepared by British Celanese<sup>94</sup> by autocondensation of crotonaldehyde with an aliphatic alcohol at 40–60° in presence of a secondary amine such as morpholine. Distillers Co.<sup>95</sup> prepare acraldehyde by interaction of  $\text{CH}_2\text{O}$  and a mixture of  $\text{MeCHO}$  and paraldehyde at 280–300° in presence of a dehydration catalyst ( $\text{Na}_2\text{SiO}_3$  and  $\text{SiO}_2$ -gel). The same firm<sup>96</sup> make 1-chloroacraldehyde by distillation of  $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CHO}$  from a dilute acid solution. Methyl vinyl ketone [but-1-en-3-one] is made in 80% yield by Imperial Chemical Industries Ltd.<sup>97</sup> by passing vaporised  $\beta$ -angelica lactone or lævulinic acid at 570–580° through a tube packed with  $\text{SiO}_2$ -chips.

E. I. Du Pont de Nemours & Co.<sup>98</sup> condense unsaturated aldehydes and ketones with thiolcarboxylic acids in presence of a basic catalyst (piperidine) to give (acylthio)-aldehydes and -ketones. Thus  $\text{CH}_2=\text{CH}\cdot\text{CHO}$  and  $\text{AcSH}$  at  $-20^\circ$ , rising to  $40^\circ$ , give a 60% yield of (3-acetylthio)propan-1-al.

*Amines, alkanolamines, amino-acids, etc.*

Improved yields of monoalkylamines such as butylamine are obtained by Sharples Chemicals Inc.<sup>99</sup> by passing a mixture of ammonia and a  $\text{C}_{1-5}$ -monohydric alcohol or an ether over an  $\text{Al}_2\text{O}_3$  catalyst coated with an oxide of Cr, Ni or Co at approximately 350°. The same firm<sup>100</sup> pass primary or secondary alcohols with ammonia and hydrogen over a metallic hydrogenation catalyst, e.g., Ni or Co, at 180–210° to obtain, e.g.,  $\text{NH}_2\text{Et}$ ,  $\text{NHEt}_2$ , and  $\text{NEt}_3$ . Usines de Melle<sup>101</sup> make alkylamines by passing the alcohol and ammonia over a dehydrogenating catalyst (reduced nickel-on-kieselguhr) to form a cyanide and then over a hydrogenating catalyst (reduced copper) to convert this into a mixture of primary, secondary, and tertiary amines by heating at 150–250°/10–40 atm. in presence of ammonia and a hydrogenation catalyst (Ni, Co, Cu chromite) promoted with an alkali or alkaline earth hydroxide or carbonate.

According to M. Senkus,<sup>103</sup> the reduction of aliphatic nitro-compounds to alkylamines proceeds better using an iron-reduction method than by catalytic hydrogenation; the  $p_{\text{H}}$  of the reduction mixture must be 3.0–3.5.

Long-chain primary aliphatic amines are dimethylated by Richards Chemical Works<sup>104</sup> by interaction with formaldehyde and aqueous formic acid in presence of an inert organic liquid such as toluene.

Imperial Chemical Industries Ltd.<sup>105</sup> claim improved yields of ethylenediamine by hydrogenating  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CN}$  at 85–130°/30–100 atm. in presence of a diluent such as ammonia and a relatively large amount of a hydrogenation catalyst. Diaminoalkanes containing one *sec.*-NH group are obtained by E. I. Du Pont de Nemours & Co.<sup>106</sup> by hydrogenating

a mixture of an alkylene dicyanide and an aldehyde or ketone in presence of reduced cobalt oxide; in this way, 1-amino-6-isobutylaminoheptane is obtained from isopropaldehyde and adiponitrile.

Alkanolamines are made by E. I. Du Pont de Nemours & Co.<sup>107</sup> by continuous or batch hydrogenation of a cyanohydrin of an aldehyde or ketone in an inert solvent and in presence of a hydrogenation catalyst; precautions are taken to limit contact between the cyanohydrin and the alkylolamine. When aliphatic polyhydric alcohols containing both a primary and a secondary OH group are heated under pressure at 120–250° with *sec.* aliphatic amines in presence of a metal oxide or metal hydrogenation catalyst (Ni), the primary OH group preferentially undergoes amination. In this way, Monsanto Chemical Co.<sup>108</sup> prepare 1-diethylaminopentane-4-ol from pentane-1 : 4-diol and diethylamine.

A modified procedure for the preparation of 2-chloroethylamine hydrochloride is described by Wingfoot Corp.<sup>109</sup>; chlorine is passed at room temperature through a solution of monoethanolamine hydrochloride in chloroform in presence of a little sulphur, the chloroethylamine hydrochloride separating.

Glycine is prepared by E. I. Du Pont de Nemours & Co.<sup>110</sup> by heating aminomethane sulphonic acid with sodium hydroxide and sodium cyanide at 50° and acidifying. J. Lincoln<sup>111</sup> prepares aminoacids by hydrolysis of the formamido esters obtained by hydrogenation (Raney nickel catalyst) of a cyano ester in presence of a formate; thus :  $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CN}$  and  $\text{HCO}_2\text{Et}$  give ethyl formamidoisobutane-2-carboxylate which is hydrolysed to aminopivalic acid.

### Aromatic intermediates

#### *Hydrocarbons, nitro- and chloro-compounds, and sulphonic acids*

Trialkylbenzenes are obtained by Mineral Oil Products<sup>112</sup> by passing methyl alkyl ketones over an  $\text{Al}_2\text{O}_3$  catalyst impregnated with phosphotungstic, silicotungstic, or phosphomolybdic acids at 200–450°.

Mixtures of trimethylbenzenes with indene and non-aromatic hydrocarbons are treated by Anglo-Iranian Oil Co.<sup>113</sup> with 65–85%  $\text{H}_2\text{SO}_4$  to remove indene and then with 96%  $\text{H}_2\text{SO}_4$  to sulphonate the aromatics; the acid layer is separated, diluted and steam-distilled to recover the trimethylbenzenes which can then be further separated into the isomeric constituents by conventional methods. Mixed xylenes are separated by Allied Chemical and Dye Corp.<sup>114</sup> by sulphonating with oleum and distilling the mixture with steam at 140–150° whereby *m*-xylene of 90.7–96% purity is obtained as distillate; the residue is cooled to 10° and the separated *p*-xylene sulphonic acid filtered and steam-distilled from 60%  $\text{H}_2\text{SO}_4$  to regenerate *p*-xylene of 94.5% purity. The advantages of this procedure over the conventional process in which the *p*-xylene is separated prior to the sulphonation by cooling to a low temperature are not stated.

Benzene hexachloride ( $\text{C}_6\text{H}_6\text{Cl}_6$ ), of course, continues to be the subject of several applications, chiefly concerned with its purification or separation of the technically valuable  $\gamma$ -isomer. Thus Imperial Chemical Industries Ltd. improve the odour of the crude product either by treatment with concentrated nitric acid<sup>115</sup> or by steam distillation to remove more volatile constituents.<sup>116</sup> Separation of the  $\gamma$ -isomer is effected by the same firm

by treatment with a solvent which preferentially dissolves the  $\gamma$ -isomer, the solution then being diluted with a second solvent to precipitate the product. Examples of suitable solvents are acetic acid (subsequently diluted with water),<sup>117</sup> a chlorinated hydrocarbon (diluted with a pentane),<sup>117</sup> and toluene or xylene (diluted with a pentane).<sup>118</sup> K. C. Kauer, R. B. Dutall, and F. N. Alquist<sup>119</sup> describe the isolation and characteristics of the  $\epsilon$ -isomer of benzenehexachloride.

The chlorination of benzene to chlorobenzene in presence of  $\text{FeCl}_3$  as catalyst has been studied in detail by R. B. MacMullen<sup>120</sup> using batch, and one-stage and multi-stage continuous processes.

Autoxygen Inc.<sup>121</sup> describe the nitration of aromatic hydrocarbons with nitric acid in which the water of reaction is removed azeotropically using either the compound being nitrated or an added inert solvent as entrainer. The method is applied to the production of nitrobenzene, nitronaphthalene, dinitrobenzene, and trinitrotoluene.

L. Leiserson, R. W. Bost, and R. Le Baron,<sup>122</sup> in studying the sulphonation of diphenyl sulphone in oleum in liquid  $\text{SO}_2$ , have found that the proportion of diphenyl sulphone increases with increased purity of the benzene.

#### *Phenols, etc.*

Socony-Vacuum Oil Co.<sup>123</sup> claim improved yields of phenol from benzene by oxidising in presence of an H-donor such as hex-1-ene or a cracked gasoline fraction. A modification of the usual catalytic reduction of quinone to hydroquinone is the use, by Société des Usines Chimiques Rhône-Poulenc,<sup>124</sup> of steam as diluent preferably with an organic substance such as benzene, chlorobenzene or ethanol. *m*-5-Xylenol is obtained by Shell Development Co. by dehydrogenation of isophorone at 400–650° in contact with activated  $\text{Al}_2\text{O}_3$  preferably in presence of a metal (Fe, Co, Cr) oxide<sup>125</sup> or an alkaline earth metal (Ca or Ba).<sup>126</sup>

The importance of the alkylation of phenols, particularly in America, is shown by the appearance of several fresh applications on this subject. Gulf Research and Development Co.<sup>127</sup> alkylate phenols with olefines containing  $\leq 3$  C atoms in presence of tetraphosphoric acid,  $\text{H}_6\text{P}_4\text{O}_{13}$ ; 3:5-di-*tert*.-butyl-*p*-cresol is thus obtained from *p*-cresol and  $\text{CH}_2:\text{CMe}_2$ . Other catalysts in similar alkylations are sulphuric acid as used by Sharples Chemicals Inc.<sup>128</sup> and boron trifluoride used by the Firestone Tyre & Rubber Co.<sup>129</sup> Universal Oil Products<sup>130</sup> use an olefine in presence of an alkyl halide and  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  as catalyst to give both C- and O-alkylated products. Thus, phenol,  $\text{CH}_3:\text{CHMe}$ , and isopropyl chloride give isopropylphenyl isopropyl ether. Hydroquinone, pyrocatechol, etc. are alkylated by Mathieson Alkali Works<sup>131</sup> with an alkyl halide in presence of zinc chloride and an alcohol such as ethanol, giving dialkyl-substituted derivatives.

Peter Spence & Sons<sup>132</sup> obtain anisole by treating phenol with methanol or dimethyl ether in the vapour phase at 175–225° and atmospheric pressure in presence of an activated  $\text{Al}_2\text{O}_3$  catalyst. At 320°, the anisole is converted into phenol, mixed cresols (chiefly *o*-), and higher methylated phenols,<sup>133</sup> whilst at still higher temperatures ( $\sim 375^\circ$ ), phenol and methanol give hexamethylbenzene.<sup>134</sup>

D. Tyrer<sup>135</sup> prepares aryl alkyl ethers by heating an alkali salt of an aryl sulphonic acid with excess of an alkali in a stream of alcohol at 250–400°. Preferably, a mixture of the Na and K salts of the sulphonic acid is used, the added alkali is lime, and the alkali sulphite formed is recovered for use in isolating the sulphonic acid from a subsequent sulphonation. A 91.5% yield of anisole is claimed from sodium and potassium benzene sulphonates.

#### *Amines and derivatives thereof*

The catalytic reduction of aromatic nitro compounds is being actively studied by Standard Oil Development Co. In one process,<sup>136</sup> the nitro-compound (specifically nitroxylenes) is passed with hydrogen and steam at 190–250°/500–3000 lb. per sq. in. through a reaction zone filled with carbon impregnated with molybdenum sulphide; the steam as water is preferably introduced at several points in the reaction chamber.<sup>137</sup> A continuous process is also described<sup>138</sup> in which the catalyst is continuously reactivated by introduction of CS<sub>2</sub> or H<sub>2</sub>S. In yet another modification the steam as diluent is replaced by a heavy hydrocarbon.<sup>139</sup>

Imperial Chemical Industries Ltd.<sup>140</sup> prepare 1 : 3 : 5-triaminobenzene and 2 : 4 : 6-triaminotoluene by hydrogenation of the nitro-compounds in presence of Raney nickel and a solvent such as ethyl acetate.

*o*-4-Xylidine is of importance for the synthesis of riboflavin and American Home Products Corp.<sup>141</sup> describe its preparation, free from isomers, by heating 4-bromo-*o*-xylene with aqueous ammonia at 195°/900–1000 lb. per sq. in. in presence of Cu<sub>2</sub>Cl<sub>2</sub>. Hoffman-La Roche Inc. describe the preparation<sup>142</sup> of aromatic amine *N*-pentosides (*e.g.*, aniline- or *o*-4-xylidine-*D*-ribosepyranoside) and their reduction<sup>143</sup> to ribitylaminobenzenes (*e.g.*, *D*-ribityl-aniline or *o*-4-xylidine).

Mixed diaminodiphenyls are made by General Printing Ink Corp.<sup>144</sup> by iron-reduction of the mixed dinitro compounds obtained by nitration of diphenyl or *o*-nitrodiphenyl. The mixture can either be used directly for the preparation of azo dyes (*cf.* p. 93), or benzidine can be separated by precipitation as sulphate.

N. V. Polak and Schwarz's Essencesfabrieken describe a number of nitro-2-alkoxyanilines (alkoxy = *n*-propoxy or *n*-butoxy) for use as sweetening agents. Several methods of preparation and separation of isomers are given in detail.<sup>145,146</sup>

The preparation and properties of the various nitro  $\alpha$ - and  $\beta$ -naphthylamines are listed by Hodgson and Hathaway.<sup>147</sup> Dey *et al.*<sup>148</sup> have studied the electrolytic reduction of *m*-nitroaniline to 2 : 4-diaminophenol using a H<sub>2</sub>SO<sub>4</sub>-electrolyte and a Pb anode; maximum yields obtained were 74% as crude sulphate or 69% as pure oxalate. Eastman Kodak Co.<sup>149</sup> prepare aminophenols by treating nitro compounds with Al and H<sub>2</sub>SO<sub>4</sub> at 80–100°; *e.g.*, nitrobenzene gives a 75% yield of *p*-aminophenol. Edwal Laboratories Inc.<sup>150</sup> hydrolyse 1 : 3 : 5-triaminobenzene with 5% HCl and obtain 3 : 5-diaminophenol. 2 : 4 : 6-Triaminotoluene similarly gives a diaminocresol.<sup>151</sup>

British Industrial Solvents Ltd.<sup>152</sup> acetylate aromatic amines using acetic acid (>20% excess) in presence of a volatile entrainer such as

benzene ; only a small proportion of entrainer is necessary as it is separated continuously from the azeotrope distilling off and returned to the reaction.

E. I. Du Pont de Nemours & Co.<sup>153</sup> claim ferric chloride to be a better catalyst than the conventional ammonium chloride-ferrous chloride for the preparation of diphenylamine from aniline.

New diazo components for azo dyes are described in several new applications. Thus American Cyanamid Co.<sup>154</sup> prepare new diazo-components for insoluble dyes by condensing a 4-nitro-4'-hydroxydiphenylamine sulphonic acid with an alkylating agent containing chlorine, reducing the 4-nitro-4'-chloroalkoxy compound and desulphonating. 4-Amino-4'-2''-chloroethoxydiphenylamine is thus obtained from 4-nitro-4'-hydroxydiphenylamine-2-sulphonic acid and the *p*-toluene-sulphonate of 2-chloroethanol. E. I. Du Pont de Nemours & Co.<sup>155</sup> describe 2-aminodiphenyl sulphones ; condensation of *o*-chloronitrobenzene with *p*-acetamidobenzene sulphinic acid in methanol in presence of sodium acetate, followed by catalytic reduction, gives 2-amino-4'-acetamidodiphenyl sulphone. J. R. Geigy<sup>156</sup> prepare 3 : 4-dichloro-5-nitro-2-aminophenol-6-sulphonic acid from 3 : 4-dichloro-2-aminophenol-6-sulphonic acid by conversion into the benzoxazolone, nitration, and hydrolysis.

Société Colorantes et Produits Chimiques Francolor<sup>157</sup> have found that when a 2-nitro-*p*-phenylenediamine is condensed with esters of acylacetic acids (*e.g.*, ethyl acetoacetate), only the NH<sub>2</sub>-group in the *m*-position to the NO<sub>2</sub> undergoes condensation. The resulting compounds, *e.g.*, 2-chloro-5-nitro-4-aminoacetoacetanilide, can be used as middle components in azo dyes. Coupling components for ice-colours, having reduced affinity are made by General Aniline & Film Corp.<sup>158</sup> by condensing *o*-hydroxy-carboxylic acids with a 4-(aminophenyl)morpholine.

#### *Miscellaneous aromatic compounds*

Carbide and Carbon Chemicals Corp.<sup>159</sup> prepare 1-phenylethanol by hydrogenation of acetophenone at 130-175°/100-150 lb. per sq. in. in presence of a mixed Cu-Cr oxide catalyst.

Standard Oil Development Co.<sup>160</sup> obtain good yields of aromatic dicarboxylic acids by catalytic oxidation of partly oxidised aromatic compounds ; thus, *o*-toluic acid is oxidised at 450° with air in presence of a V<sub>2</sub>O<sub>5</sub>-catalyst to give an 85% yield of phthalic acid. The oxidation of vanillin to vanillic acid has received some attention. Thus, the Institute of Paper Chemistry carry out the oxidation either by heating vanillin in alkaline medium with an oxide of silver or gold,<sup>161</sup> or by fusing vanillin with a mixture of sodium and potassium hydroxides at 180°.<sup>162</sup> C. J. Lintner and L. M. Parks<sup>163</sup> describe its preparation by oxidation of vanillin in 20% aqueous NaOH with Ag<sub>2</sub>O or AgNO<sub>3</sub> at 50-80°.

Modified methods of preparing chlorinated quinones such as chloranil and 2 : 3-dichloro-1 : 4-naphthaquinone are described by the United States Rubber Co. They chlorinate amines (or derivatives thereof)<sup>164</sup> or phenols or naphthols<sup>165</sup> in a mixture of sulphuric acid and, preferably, acetic acid. Good yields are claimed of chloranil both from aniline and phenol.

*Polynuclear and heterocyclic compounds*

A very large number of applications have appeared during the last few years relating to heterocyclic compounds. The majority, however, are products having chemotherapeutic properties and, as such, are really outside the scope of this review; these include acridine, pyrimidine and quinoline derivatives as antimalarials, sulphanilamide derivatives of thiazoles, pyrazines, etc., compounds related to biotin and penicillin etc. New heterocyclic intermediates for photographic cyanine dyes are also the subject of several applications.

Imperial Chemical Industries Ltd.<sup>166</sup> obtain 2-aminopyrroline 1-oxides by hydrogenation of  $\alpha$ -nitrocycanoalkanes in a solvent (EtOH) and in presence of Raney nickel or palladium; e.g., 1-nitro-1-2'-cyanoethyl-cyclohexane gives 2-amino-5:5-pentamethylenepyrroline 1-oxide. Société des Usines Chimiques Rhône-Poulenc<sup>167</sup> oxidise but-1-yn-3-ol to but-1-yn-3-one, with chromic acid, and then condense with a guanidine salt in sulphuric acid to give 2-amino-4-methylpyrimidine.

There are several applications relating to piperazine: Société des Usines Chimiques Rhône-Poulenc prepare it by heating monoethanolamine at 220–250° in presence of a dehydration catalyst such as  $MgCl_2$ <sup>168</sup> and isolate it as the sparingly soluble double salt with ammonium chloride<sup>169</sup>; American Cyanamid Co.<sup>170</sup> pass  $OH \cdot [CH_2]_2 \cdot NH \cdot [CH_2]_2 \cdot NH_2$  over a catalyst such as activated  $Al_2O_3$  at 400–500°.

Merck & Co. have several processes for preparing 2-aminopyrazines, optionally substituted at positions 5 and/or 6 by alkyl, aryl, etc. Thus the corresponding (alkyl or aryl) lumazine is heated with conc.  $H_2SO_4$  at 180–245°,<sup>171</sup> or is treated with an alkali hydroxide to give either a 2-amino- or 2-hydroxy-pyrazine-3-carboxylic acid, depending on the quantity of alkali used, and then decarboxylation is effected by heating alone or in a solvent such as nitrobenzene or  $H_2SO_4$ .<sup>172</sup> Alternatively, the carboxylic acid is converted through an ester to the amide which is treated with a hypochlorite.<sup>173</sup>

Society of Chemical Industry in Basle<sup>174</sup> describe sulphonated 1-alkyl-, 1-aryl-, or 1-aralkyl-benziminazoles carrying at position 2 a group containing  $\leq 4$  conjugated double linkings. Thus, o-phenylenediamine is condensed with fumaric acid and the resulting 1:2-di-(2'-benziminazyl)-ethylene is sulphonated. Alternatively, the corresponding 1:2-di-(2'-benziminazyl)ethane can be oxidised with a mild oxidising agent such as  $Fe_2(SO_4)_3$  in a mineral acid, or mercuric acetate in acetic acid.<sup>175</sup> The products show a blue fluorescence, have an affinity for cellulose fibres, and are used as optical bleaching agents. Other optical bleaches are described by J. R. Geigy A.-G.<sup>176</sup> who treat, for example, 4:4'-di-(2'':4''-diamino-s-triazin-6''-ylamino)stilbene-2:2'-disulphonic acid with formaldehyde.

A new type of heterocyclic compound, for use as a colour-former in colour photography, is prepared by General Aniline & Film Corp.<sup>177</sup> by condensing a 1-substituted 3-amino-5-pyrazolone with diketene in an inert solvent. Thus 3-amino-1-phenyl-5-pyrazolone gives 4:3'-diketo-2'-phenyl-6-methyl-4:2':3':4'-tetrahydropyrazolo-1':5'-1:2-pyrimidine.

Francolor<sup>178</sup> describe the preparation of a number of 6- and 5-amino-benzthiazoles substituted at position 2 by alkyl, alkoxy, etc., and their condensation with esters of acylacetic acids to give valuable coupling components for insoluble azoic dyes.

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## AZO DYES (E. L. Johnson, B.Sc., Ph.D., A.R.I.C.)

THIS review which takes the form adopted in previous years covers a two-year period (November, 1946, to October, 1948, inclusive) for dyes for wool, leather, and cellulose acetate rayon, and for lakes and pigments, these topics having been omitted last year. Owing to continued restriction of space a review of patents for dyes for cotton (including the azoic type) is postponed until next year.

There has been a marked increase in the number of patent specifications requiring review; for example, about fifty (covering a two-year period) dealing with dyes for wool and leather are reviewed here compared with only four in 1946. The principal research activity as indicated by patent publications has concerned dyes for cotton, wool, and cellulose acetate rayon, and has, in the main, followed familiar lines. There are no major advances to report. In the field of wool dyes, the main emphasis has been on metal-containing and metallisable dyes. With regard to dyes for cellulose acetate rayon, the intense patenting activity of the Eastman Kodak Co. which has been a conspicuous feature of recent years has shown some tendency to diminish towards the end of the period under review. Imperial Chemical Industries Ltd. have a series of specifications dealing with water-soluble dyes of improved exhaustion when applied to cellulose acetate rayon from the dilute liquors used in dyeing on winch machines.

Attention is drawn to the publication of an index<sup>1</sup> (in four volumes) to microfilms available at the Board of Trade recording the several thousand dye manufacturing processes of the I.G. Farbenindustrie A.-G. The index is divided into two sections, the first (Vols. I and II) being an alphabetical list of dyes, and the second (Vols. III and IV) a list of dyes classified according to type, references being given, where possible, to Schultz's "Farbstofftabellen." Each dye is listed as an individual chemical, no blends being included.

The minutes<sup>2</sup> of certain conferences of an I.G. inter-factory scientific commission (Wissenschaftlichen Ako) for discussing speculative azodye research carried out in their factories were referred to in last year's review.<sup>3</sup> The full reports<sup>4</sup> of the work which formed the subjects of these conferences during the years 1936 to 1941 are now available as microfilm copies at the Board of Trade.

## General

The mechanism of the decomposition reactions of diazo compounds has continued to be a matter for dispute. H. H. Hodgson,<sup>5</sup> replying to the criticisms of K. H. Saunders and W. A. Waters,<sup>6</sup> has provided a mechanism based on simple electronic theory and regards as unnecessary the free radical hypothesis of the latter authors. The free radical concept has been defended by D. H. Hey and W. A. Waters<sup>7</sup> who allege that Hodgson has applied it to experimental conditions their theory was never intended to embrace. They agree that the decompositions can take either a homolytic or a heterolytic course according to circumstances, and that occasionally both processes may occur simultaneously, but they consider that the experimental evidence establishes beyond dispute the part played by free radicals in the cases they discuss.

Recent investigations on the introduction of the azo group by methods not involving a diazo coupling reaction include that of M. Martynoff,<sup>8</sup> who has condensed nitrobenzene with an alkoxyaniline in presence of  $\text{Na}_2\text{CO}_3$  to give an alkoxyazobenzene (*o*-anisidine gave 60% of *o*-methoxyazobenzene) which could then be dealkylated with aluminium chloride to give the hydroxyazobenzene;  $\alpha$ - and  $\beta$ -naphthylamines with nitrobenzene under similar conditions give 1- and 2-benzeneazonaphthalenes. The same author<sup>9</sup> has condensed nitrobenzene with diamines in presence of powdered sodium hydroxide to give aminoazo compounds, *o*-phenylenediamine giving 80% of 2-aminoazobenzene. The preparation of a number of symmetrical azo compounds in about 80% yield by the rapid decomposition of diazo compounds with cuprous chloride has been described by B. M. Bogolovskii.<sup>10</sup>

P. Ruggli and E. Iselin<sup>11</sup> have condensed *p*-dinitrosobenzene with 2.5 mols. of *p*-nitroaniline in boiling acetic acid to give *p*-bis-(*p*'-nitrobenzeneazo)benzene and the corresponding azoazoxy compound in an inseparable mixture which yields the pure bisazo compound on reduction. Attempts by the same authors<sup>12</sup> to prepare *p*-nitrosoazobenzene by mild reduction of *p*-nitroazobenzene always resulted in *p*-nitrohydrazobenzene.

The observations of J. S. P. Blumberger<sup>13</sup> that the restriction of resonance by vicinal substitution in certain azo dyes causes a marked hypsochromic effect has lead H. H. Hodgson<sup>14</sup> to question the structure of the so-called *cis*-azobenzene described by G. S. Hartley.<sup>15</sup> This compound is bathochromic compared with *trans*-azobenzene contrary to the view that the more strained *cis*-structure should be hypsochromic, and Hodgson considers that its properties are more in harmony with those of a double compound of azoxybenzene and hydrazobenzene.

Continuing an investigation of azo dyes derived from 1-amino-5-naphthol, A. E. and B. A. Porai-Koshits and V. V. Perekalin<sup>16</sup> have confirmed that the products obtained by coupling with diazobenzene are the 2-, 6-, and 8-phenylazo derivatives according to the  $p_H$  of coupling (cf. Ann. Repts. 1947, **32**, 61); H-acid gives the 4-azo compound at  $p_H$  below 4 and the 8-azo compound at higher  $p_H$  values. V. V. Perekalin<sup>17</sup> by summation of the resonance energies of each substituent has calculated the comparative activities of the carbon atoms in some aminonaphthol sulphonic acids and in their mono-*o*-aminoazo derivatives and thence has deduced whether they are capable of forming bisazo derivatives. Experimental confirmation of the predictions has been obtained in some cases; thus the 4- and 7-sulphonic acids of 1-amino-5-naphthol couple once only, whilst the 6- and 8-sulphonic acids couple twice.

Azo compounds containing boronic acid groups for use in physiological investigations have been prepared by H. R. Snyder and C. Weaver<sup>18</sup> using *m*-aminobenzenboronic acid as a diazo component and *m*-hydroxy- and *m*-dimethylamino-benzenboronic acid as coupling components. H. R. Snyder and S. L. Meisel<sup>19</sup> have prepared azo dyes from benzidine-2:2'-diboronic acid and conventional coupling components including H-acid which gives an analogue of Trypan Blue (Colour Index No. 477). These dyes are unlikely to be of interest for textile purposes owing to the comparative instability of the boronic acid group.

The preparation of iodine-containing azo dyes for investigation as radiographic opaque agents has been described by H. Bang and C. F. Martin<sup>20</sup> and H. Bang<sup>21</sup> who have prepared, for example, the Congo Red analogue from 3 : 3' : 5 : 5'-tetraiodobenzidine.

A method of preparing facsimile records patented by the Radio Corporation of America<sup>22</sup> consists in electrolysing paper etc., impregnated with an alkaline solution of a sulphonated primary aromatic amine, a nitrite, a water-soluble inorganic salt as additional electrolyte, and one or more coupling components whereby generation of an acid reaction at an anode results in local formation of azo compounds; in an alternative process,<sup>23</sup> the impregnating solution contains a diazonium compound, an inorganic salt, an acidic reducing agent (e.g., tartaric acid), and a coupling component, colour development following generation of an alkaline reaction at a cathode on electrolysis.

Continuing an investigation of the bisulphite compounds of azo dyes, V. M. Ufimtsev<sup>24</sup> has reacted the bisulphite compound of 1-benzeneazo-2-naphthol with phenylhydrazine to give the corresponding 2-hydrazide; this is oxidised with nitrous acid to 1 : 2-bis(benzeneazo)naphthalene which gives 2-phenylnaphthotriazole with sulphuric acid and the corresponding 5-sulphonic acid with aqueous alcoholic sodium bisulphite. 1-Benzeneazo-4-naphthol reacts similarly. The dye sulphanilic acid → 2-naphthol-4-sulphonic acid on boiling with sodium bisulphite yields 1-amino-2-naphthol-4-sulphonic acid *via* the 1-sulphamyl derivative.

The product of the reaction of diazotised aminoguanidine with  $\beta$ -naphthol, tentatively formulated by R. N. Shreve, R. P. Carter and J. M. Willis<sup>25</sup> as 1-guanidinoazo-2-naphthol, has been shown by reductive fission methods by J. Reilly, J. Teegan and M. Carey<sup>26</sup> to be 1-(tetrazole-5-)azo-2-naphthol, which is formed from each of three distinct diazonium complexes formed by the action of sodium nitrite on aminoguanidine.

Azo compounds have continued to attract attention for investigation of relations between absorption spectra and molecular structure. (Mme.) P. Ramart-Lucas, (Mme.) T. Guilmart and M. Martynoff<sup>27</sup> have shown by spectroscopic studies that acylation of azonaphthols gives *O*-acyl rather than *N*-acyl derivatives even with those dyes which normally exist in solution largely as quinone-hydrazones. Similar study of hydroxyazo compounds by (Mme.) P. Ramart-Lucas and M. Martynoff<sup>28</sup> has shown that in the case of *ortho* derivatives there exists besides the azophenol and quinone-hydrazone forms a third form which is attributed to a displacement of the electronic configuration of one of the nitrogen atoms of the azo group.

An investigation by W. R. Brode and R. J. Morris of the absorption spectra of symmetrical<sup>29</sup> and unsymmetrical<sup>30</sup> disazo dyes derived from benzidine has shown that establishment of non-coplanar conditions for the benzidine nucleus causes insulation of the two chromophores and enables each half-structure to show an independent absorption. The molecular conjugation is progressively inhibited by the introduction of unreactive methyl groups in the 2 : 2' and 6 : 6' positions of the benzidine nucleus, the tetramethyl compound showing, apparently, almost complete insulation of the two halves.

M. P. Grammaticakis<sup>31</sup> in an investigation of 1 : 2-disubstituted hydrazines and their oxidation products has found that substitution of the methane hydrogen atoms of methaneazobenzene with one or two phenyl radicals effects a feeble shift in absorption towards the visible spectrum.

The colour reactions of certain classes of azo dyes with copper salts in very dilute aqueous solution have been tabulated by W. A. Alexander.<sup>32</sup> Dyes showing a marked colour change (from pink or red to yellow-brown) are 2-azo derivatives of 1-naphthol-4- and/or 5-sulphonic acids or 1-azo derivatives of 2-naphthol-3- and/or 6-sulphonic acids (the 8-position may be substituted with -OH or -SO<sub>3</sub>H) whilst other closely related compounds are insensitive; there is no correlation between this property and ability of the dyes to form copper complexes.

### Dyes for wool and leather

The majority of patent specifications to be reviewed dealing with azo dyes for wool make provision for conversion of the dyes to metal-complexes either in substance or on the fibre.

Dyes not intended for metallisation at any stage include the yellow dyes of excellent fastness to milling, perspiration, alkalis, and light made by Sandoz Ltd.<sup>33</sup> by coupling a diazotised aniline-3-sulphonacylamide (acyl = residue of a saturated or unsaturated fatty acid of 11 C or more), which may have alkyl or alkoxy in position 4, with the usual 1-sulphoaryl-5-pyrazolone coupling components. Pyrazolone dyes are made by J. D. Kendall and D. J. Fry<sup>34</sup> by treating in strong alkali at least two equivalents of a diazo compound with a compound of the type, CHRR'-CH<sub>2</sub>-CO<sub>2</sub>R'', where R and R' are groups promoting enolisation such as CH<sub>3</sub>-CO, CN, or CO<sub>2</sub>Et; e.g., Tartrazine is obtained by reacting diazotised sulphanilic acid with a caustic-alkaline solution of CO<sub>2</sub>Et-CHAc-CH<sub>2</sub>-CO<sub>2</sub>Et and hydrolysing the isolated product.

Red dyes are obtained by E. I. Du Pont de Nemours & Co. by coupling gamma acid or an *N*-alkyl derivative under acid conditions (a)<sup>35</sup> with a diazotised *o*-aminodiphenylsulphone carrying an acylamido or sulphonamido group in the nucleus devoid of the amino group, and (b)<sup>36</sup> with diazotised 4- (or 5-)chloro- (or -bromo-)acetyl- (or -propionyl-)aminoaniline-2-sulphonic acid.

Navy-blue dyes of the well-known Sulphon Cyanine type (metanilic acid →  $\alpha$ -naphthylamine → 1-arylamino-naphthalene-8-sulphonic acid, Colour Index No. 289), but having better levelling properties, somewhat better light fastness, usually purer shades, and often better shades in artificial light are made by J. R. Geigy A.-G.<sup>37</sup> using sulphonyl esters of metanilic acid instead of metanilic acid as first component. Black dyes fast to milling, perspiration, sea-water, and light made by the General Aniline and Film Corporation<sup>38</sup> are of the type: aminodiphenyl ether →  $\alpha$ -naphthylamine → 2-naphthol-4-sulphonic acid (which may have chloro or acylamido in the 6- position).

Société Anonyme de Matières Colorantes et Produits Chimique Francolor<sup>39</sup> (hereafter called Francolor) use acylacetaryl amides, CH<sub>2</sub>Acyl-CO-NH-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)-NH<sub>2</sub>-1 : 3 : 4, as middle components (M) in dyes A → M → E, where A is a sulphonated diazo component, and A and E together contain at least two sulphonic acid groups; the products

are acid wool dyes reserving cellulose fibres. Novel diazo components used by the American Cyanamid Co. with, *e.g.*, pyrazolone coupling components are aminosulphoaryl derivatives of benzodioxan<sup>40</sup> and benzocoumaran,<sup>41</sup> whilst the Eastman Kodak Co.<sup>42</sup> use diazotised 4-amino-fluoranthrene for coupling with naphthylamine-, naphthol-, or aminonaphtholsulphonic acids.

In the metallisable dye class, attention continues to be directed towards compounds suitable for dyeing wool by the single-bath chroming process. Such dyes giving bordeaux shades fast to water and light are obtained by Imperial Chemical Industries Ltd.<sup>43</sup> by coupling diazotised 4-chloro- (or -methyl-) 2-aminophenol-6-sulphonic acid with a 1-phenyl-5-pyrazolone-3-carboxyarylamide, aryl being phenyl with one or more alkyl or halogen substituents, or naphthyl. The same firm obtain orange to red shades<sup>44</sup> from an *o*-aminophenolmonosulphonic acid  $\rightarrow$  1-3': 4'-dichlorophenyl-3-methyl-5-pyrazolone, and a black shade<sup>45</sup> from (specifically) 4-nitro-2-aminophenol-6-sulphonic acid  $\rightarrow$  6-bromo-2-naphthol.

A method of the Society of Chemical Industry in Basle for temporary solubilisation originally applied to azoic-type pigments for cellulosic fibres<sup>46</sup> has now been applied by them to *oo'*-dihydroxymonoazo compounds devoid of solubilising groups and containing a nitro group or at least two halogen atoms<sup>47</sup>; these compounds are allowed to react in presence of a tertiary base with an organic acylating agent containing at least one salt-forming group to give ester-like substances. The products in the form of their water-soluble alkali salts dye wool<sup>48</sup> by the single-bath chroming process which effects simultaneous metallisation and hydrolysis of the ester group (with loss of the solubilising function). For example, the dye 4-chloro-2-aminophenol  $\rightarrow$  5:8-dichloro-1-naphthol acylated with *m*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl dyes wool by the one-bath chroming process a reddish-blue. The compounds of the earlier patent<sup>46</sup> required alkaline hydrolysis.<sup>49</sup>

J. R. Geigy A.-G.<sup>50</sup> prepare dyes suitable for the single-bath chroming process by coupling diazotised 4-chloro-2-aminophenol-6-sulphonic acid with a 1-carbalkoxyamino-7-naphthol. The same coupling components are used by Sandoz Ltd.<sup>51</sup> for dyes from *o*-aminophenol-sulphonic acid diazo components in general, but excluding the specific component of the above case, the products being suitable for chromium-complex formation in substance or on the fibre by the one- or two-bath process. Bluish-grey shades are obtained in each case.

Among dyes more suitable for the after-chrome process are those obtained by J. R. Geigy A.-G.<sup>52</sup> by coupling a diazotised *N*-[3-amino 4-(X)benzoyl]aminosalicylic acid (X = halogen, SO<sub>3</sub>H, or SO<sub>2</sub>Arlyl) with gamma acid or an *N*-alkyl derivative; they give red shades which show little change on after-chroming. Dyes obtained by the same firm by coupling a diazotised 2-aminophenol-6-sulphonic acid carrying a *cycloalkyl* or alkyl (C<sub>3</sub> to C<sub>8</sub>) group in position 4 with a pyrazolone devoid of solubilising groups dye wool yellow, afterchromed to red shades of good wet- and light-fastness.<sup>53</sup>

Dyes obtained by J. R. Geigy A.-G.<sup>54</sup> by condensing a 4-nitrobenzene-azosalicylic acid with an aminodiphenylamine in presence of sodium

hydroxide, and which are probably azoxy compounds, are useful for dyeing wool (by the afterchrome process), leather, and for chrome-printing on cotton. Hexylresorcinol (E) is used by the American Cyanamid Co.<sup>55</sup> as coupling component for mono-, dis-, and tris-azo dyes suitable for animal and vegetable fibres, e.g., 4-nitro-2-aminophenol  $\rightarrow$  E  $\leftarrow$  4-aminoazobenzene-4'-sulphonic acid.

Frequently provision is made in patent specifications for metallisation either in substance or on the fibre and a number of metals may be specified, e.g., iron, cobalt, nickel, and copper as well as chromium, but there seems to be little tendency to use metals other than chromium in practice. Dyes chromable in substance or on the fibre and giving fast olive to greyish-green shades are made by the Society of Chemical Industry in Basle<sup>56</sup> by coupling an *o*-diazophenol with a monoalkyl ether of 2:6-dihydroxynaphthalene; e.g., the chromium complex of 6-chloro-2-aminophenol-4-sulphonic acid  $\rightarrow$  6-methoxy-2-naphthol gives greyish-green shades on wool; the products may also be used for chrome-printing on cotton. Dyes of similar properties giving reddish-blue to olive shades are obtained by the same firm from a sulphonated *o*-diazophenol and a 1-naphthol containing alkyl (of more than one carbon atom) or *cycloalkyl* in position 4;<sup>57</sup> e.g., 4-nitro-2-aminophenol-6-sulphonic acid  $\rightarrow$  4-*n*-butyl-1-naphthol gives greenish-olive shades on wool by either the single-bath chrome or afterchrome process.

J. R. Geigy A.-G.<sup>58</sup> couple a diazotised amine having a complex-forming group in the *ortho* position with a 1-naphthol-8-sulphonic acid having SO<sub>2</sub>R or COR (R = alkyl, *cycloalkyl*, aryl) in position 4. The products, after conversion to metal complexes in substance or on the fibre, give deeper shades and sometimes better light fastness than those having a sulphonamide group in position 4. The same firm couple a diazotised diaryl ketone having a diazotisable amino group in one aryl nucleus and an *o*-hydroxycarboxy grouping in the other with any suitable coupling component.<sup>59</sup> The components may be selected so that the dye contains a metallisable azo system, and the dyes may be metallised in substance or on the fibre, but it is better to restrict metallisation in substance to a portion only of the complex-forming groups and to complete metallisation on the fibre. The dyes may be used for animal or vegetable fibres according to constitution, but chromable wool dyes from 5-pyrazolones are specially noted; e.g., 3-amino-4'-hydroxy-3'-carboxybenzophenone  $\rightarrow$  1-(2'-chloro-5'-sulphophenyl)-3-methyl-5-pyrazolone dyes wool a greenish-yellow, the wet-fastness being improved by afterchroming.

Level-dyeing dyes for metallisation in substance or on the fibre giving yellow shades fast to washing, milling, and light are obtained by E. I. Du Pont de Nemours & Co.<sup>60</sup> by coupling diazotised 3:6-dichloro-2-aminophenol-4-sulphonic acid with an unsulphonated pyrazolone coupling component. The American Cyanamid Co. couple a diazotised amine having a complex-forming group in the *ortho* position with a 3-amino-5-pyrazolone and use the products for metallisation in substance<sup>61</sup> or on the fibre.<sup>62</sup>

There are a number of cases involving the use of *o*-hydroxy- (or carboxy-) *o*'-aminoazo metallisable system. Brown dyes related to

Metachrome Brown B (Colour Index No. 101) and suitable for the afterchrome process are obtained by the Society of Chemical Industry in Basle<sup>63</sup> by coupling a diazo component carrying a complex-forming group with a 2:4-diaminobenzenesulphonamide or 2:4-diaminophenyl alkyl sulphone. Yellowish-green dyes prepared by the same firm are the chromium complexes of an *o*-aminophenolsulphonic acid  $\rightarrow$  a 2-naphthylamine carrying an alkoxy group.<sup>64</sup> Yellowish-green shades are also obtained by J. R. Geigy A.-G.<sup>65</sup> by chroming on wool a 3-amino-4-hydroxybenzophenone-3'-sulphonic acid  $\rightarrow$  2-amino-3-naphthoic acid.

When dyeing wool with the chromium complexes of *o*-hydroxy- (or -carboxy-) *o'*-aminoazo compounds the American Cyanamid Co.<sup>66</sup> obtain fuller, brighter, and more reproducible shades by having present in the dyebath a trivalent chromium salt equal in amount to about 5% of the weight of dye used. They have also found that the addition of aldehydes or aldehyde-generating substances to the dyebath prevents the demetallisation of such complexes during dyeing.<sup>67</sup> Harshness and tendering of wool during dyeing, stripping, and re-dyeing in an 8% sulphuric acid bath is also prevented by the presence of aldehydes.

The American Cyanamid Co. prepare the chromium complexes of the dyes obtained by coupling (a)<sup>68</sup> a 4-diazo-1-sulphophenyl-5-pyrazolone with a coupling component giving rise to a metallising group in the *ortho* position to the azo group, and (b)<sup>69</sup> a 4-diazo-1-phenyl-5-methyl-3-pyrazolone with coupling components such as R-acid and amino-R-acid. The same firm<sup>70</sup> prepare compounds metallisable in substance or on the fibre by the use of acylacetoneitriles as coupling components. R. S. Long<sup>71</sup> of this firm has reported an investigation of the properties of dyes from diazotised sulphonated amines having hydroxyl or carboxyl in the *ortho* position and acylacetoneitriles. These dyes form chromium complexes which are shown to contain one atom of chromium for each molecule of dye, the complexes having usually much greater colour value than the unmetallised dyes, many of which have practically none when applied to wool as acid dyes. The same firm has prepared the chromium complex of 4-chloro-2-aminophenol-6-sulphonic acid  $\rightarrow$  2S-acid which dyes wool a bright blue, the shade being retained in artificial light.<sup>72</sup>

A series of chrome-complex dyes for wool having excellent levelling and fastness properties has been obtained by E. I. Du Pont de Nemours & Co.<sup>73</sup> by coupling the diazo oxide of 3:6-dichloro-2-aminophenol-4-sulphonic acid, obtained from 2:5:6-trichloroaniline-3-sulphonic acid, with a coupling component containing at least one sulphonic acid or sulphonamide group and then converting into the chromium-complex. Dyes of J. R. Geigy A.-G.<sup>74</sup> suitable for dyeing silk from a neutral dyebath in shades fast to washing and light are the copper complexes of dyes of the pattern, *o*-amino-phenol- (or -naphthol-)sulphonic acid  $\rightarrow$  resorcinol  $\leftarrow$  unsulphonated amine.

J. R. Geigy A.-G.<sup>75</sup> have found that the use of a chromium-complex of a salicylic acid, usually ammonium chromium salicylate, as metallising agent for preparing chrome-complexes in substance enables milder reaction conditions to be employed so that decomposition (e.g., hydrolysis of amide or ester groups) of the parent dye is avoided.

New dyes for leather are still being made by exploiting the cheap, readily available, traditional azo components. Williams (Hounslow) Ltd. have three specifications for grey to black hexakisazo dyes for leather. In the first,<sup>76</sup> the dyes are unsymmetrical of the type:  $A^1 \rightarrow \text{H-acid} \leftarrow D^1 \rightarrow Z \leftarrow D^2 \rightarrow \text{H-acid} \leftarrow A^2$ , where  $A^1$  and  $A^2$  are primary aromatic amines, sulphonated or not,  $D^1$  and  $D^2$  are benzidine-type diamines, and  $Z$  is an *N*-substituted *m*-aminophenol or one of certain other twice-coupling compounds, the structures being made unsymmetrical either by the use of different  $A$  or  $D$ , or by having the acid and alkaline couplings on to the two mols. of *H*-acid in reverse order with respect to  $A$ . In the second<sup>77</sup> they are of the type:  $(A \xrightarrow{\text{acid}} \text{H-acid} \xleftarrow{\text{alk}} D)_2 \rightleftharpoons Z$ , and in the third<sup>78</sup> of the type:  $(A \xrightarrow{\text{alk}} \text{H-acid} \xleftarrow{\text{acid}} D)_2 \rightleftharpoons Z$ , both types being symmetrical. The same firm make grey to black heptakisazo dyes of the pattern  $(A^1 \xrightarrow{\text{alk}} \text{H-acid} \xleftarrow{\text{acid}} D)_2 \rightleftharpoons Z^1 \leftarrow A^2$ , where  $A^1$ ,  $A^2$  and  $D$  have the same significance as above and  $Z^1$  is a compound capable of coupling three times, such as *m*-phenylenediamine, resorcinol, *m*-aminophenol, or a *m*-hydroxydiphenylamine.<sup>79</sup> An example of the last specification is:  $(\text{aniline} \xrightarrow{\text{alk}} \text{H-acid} \xleftarrow{\text{acid}} \text{benzidine})_2 \rightleftharpoons m\text{-hydroxydiphenylamine} \leftarrow \text{sulphanilic acid}$ , which gives blue-grey shades in weak dyeings on vegetable-tanned leather and neutral black shades on chrome-tanned leather.

Imperial Chemical Industries Ltd.<sup>80</sup> prepare the trisazo dye, salicylic acid  $(1) \leftarrow$  benzidine  $(3) \rightarrow$  resorcinol  $(2) \leftarrow$  aniline-2 : 5-disulphonic acid, which gives level orange-brown shades on leather of good fastness properties and free from marking-off defects. They also obtain orange-brown shades of good fastness properties and stable to  $p_H$  changes from dyes of the pattern: a 1-sulphophenyl-3-methyl-5-pyrazolone (the phenyl nucleus of which may be substituted by halogen or alkyl)  $\leftarrow$  benzidine  $\rightarrow$  a twice-coupling 1 : 3-diaminobenzene  $\leftarrow$  an arylamine sulphonie acid devoid of OH groups.<sup>81</sup> They obtain grey to black shades from the dye, *m*-aminophenol  $(3) \leftarrow$  benzidine  $(1) \xrightarrow{\text{acid}} \text{H-acid} \xleftarrow{(2) \text{ alk}} \text{sulphanilic acid}$ .<sup>82</sup>

The Society of Chemical Industry in Basle<sup>83</sup> prepare metal complexes of dyes of the pattern:  $A^1 \rightarrow 1 : 3\text{-dihydroxynaphthalene} \leftarrow A^2$ , where  $A^1$  and  $A^2$  are primary arylamines free from azo groups at least one of which carries a complex-forming group. The products, particularly the iron-complexes, are especially useful for dyeing leather.

### Dyes for cellulose acetate rayon

Patent specifications relating to dyes for cellulose acetate rayon frequently mention other synthetic fibres for which they can be used, e.g., superpolyamides such as Nylon and fibres composed of vinyl-type polymers or co-polymers.

For yellow-shade dyes, *ortho* coupling phenols continue to be exploited. E. I. Du Pont de Nemours & Co.<sup>84</sup> prepare the dye, *p*-aminoacetanilide  $\rightarrow$  *p*-chlorophenol, by using *p*-nitroaniline as diazo component and, after coupling, reducing the nitro group and acetylating. The Eastman Kodak Co. couple *p*-cresol with diazo components of the type:  $(a)^{85}$   $p\text{-OR}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  ( $R$  = alkyl, hydroxyalkyl, or alkoxyalkyl)

or  $p\text{-R'CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  ( $\text{R}' = \text{H}$ , or hydroxyalkyl), and (b)<sup>86</sup>  $p\text{-NR''R'''}\cdot\text{CXY}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  ( $\text{R}'' = \text{H}$ , alkyl, or substituted alkyl;  $\text{R}''' = \text{R}''$  or acyl;  $\text{X}, \text{Y} = \text{H}$  or alkyl). The Society of Chemical Industry in Basle<sup>87</sup> use, with *ortho*-coupling phenols, diazo components which are benzenoid amines having, *para* to the amino group, an *O*-alkylene group joined again to the benzene ring through O, so forming a heterocyclic ring condensed on to the benzene ring in the 3 and 4 positions, to obtain yellow insoluble dyes of high wet and light fastness, e.g., 3:4-methylenedioxyaniline  $\rightarrow$  *p*-cresol. Fast yellow dyes are obtained by British Celanese Ltd.<sup>88</sup> by alkylating dyes obtained by coupling a diazotised nitroaniline with a phenol, e.g., 4-chloro-2-nitroaniline  $\rightarrow$  phenol, ethylated.

Water-soluble non-phototropic yellow dyes obtained by the Society of Chemical Industry in Basle<sup>89</sup> are the acid esters of a polybasic acid (e.g., sulphuric, succinic) and dyes made by coupling a diazotised aminophenyl hydroxyalkyl sulphone with yellow-forming components, e.g., the sulphuric ester of  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$   $\rightarrow$  1-2'-chlorophenyl-3-methyl-5-pyrazolone. Imperial Chemical Industries Ltd.<sup>90</sup> make water-soluble yellow dyes, showing good exhaustion when applied to cellulose acetate rayon from the dilute liquors used in winch machines, of the pattern: *m*- or *p*-aminophenyl hydroxyalkyl ether sulphuric ester  $\rightarrow$  2- or 3-hydroxydibenzfuran.

The Eastman Kodak Co.<sup>91</sup> couple a diazotised 3-nitro-4-aminobenzene-sulphonalkylamide, which may have halogen in position 5, with a 5-pyrazolone having H or alkyl in position 1, e.g., 3-nitro-4-aminobenzenesulphonyl-*N*-ethylamide  $\rightarrow$  3-methyl-5-pyrazolone. They also couple diazotised 2-nitro-4-thiocyananiline with a 3-carbalkoxy-5-pyrazolone to give greenish-yellow dyes with an orange tint and very fast to light.<sup>92</sup> The Eastman Kodak Co.<sup>93</sup> also use a  $\beta$ -ketocyclo-butyl (or -amyl) sulphoxide or sulphone as a coupling component to give mainly yellow dyes, e.g., *o*-anisidine  $\rightarrow$   $\beta$ -ketocyclobutyl sulphone [3-ketotetrahydrothiophen 1:1-dioxide] which gives greenish-yellow shades on cellulose acetate rayon; dyes suitable for wool may be prepared from sulphonated diazo components.

Non-phototropic golden-yellow shades of good light-fastness are obtained by British Celanese Ltd.<sup>94</sup> from azobenzene derivatives containing an amino group *para* to the azo group and three or four substituents (excluding nitro) *ortho* to the azo group, e.g., 2:6-dichloro-4-amino-2':6'-dimethyl-4'-methoxyazobenzene from 2:6-dichloro-4-nitroaniline  $\rightarrow$  *m*-5-xylenol by methylation and reduction of the nitro group.

Many dyes for cellulose acetate rayon in the orange to blue shade range are of the pattern: *p*-nitroamine of the benzene series (A)  $\rightarrow$  *para*-coupling secondary or tertiary amine of the benzene series (E). Occasionally the coupling component is a naphthylamine or a heterocyclic compound containing a secondary or tertiary N atom in the ring. A is frequently substituted in the 2 and/or 6 positions with respect to the amino group with groups such as halogen, nitro, cyano, and sulphonamide, whilst E may be substituted in the 2 and/or 5 positions with respect to the amino group with groups such as alkyl, alkoxy, halogen, and acylamino.

The Eastman Kodak Co. have a series of specifications which provide for variations of the *N*-substituents of E. Thus they use di- or trihydroxy-*N*-arylpiperidines in which one of the hydroxyl groups may be alkylated or esterified to obtain dyes such as *p*-nitroaniline  $\rightarrow$  3:5-dihydroxy-*N*-*m*-tolylpiperidine (red).<sup>95</sup> The coupling component *N*-2-(2'-hydroxyethoxy)ethyl-*o*-chloroaniline is used for dyes with the usual diazo components, e.g., orange with diazotised *p*-nitroaniline.<sup>96</sup> Dyes containing carbonamide groupings in an aliphatic side chain are obtained from coupling components,  $\text{NR}(\text{Aryl})\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot\text{NR}'\text{R}''$  (*R*, *R'*, *R''* = H or alkyl; *n* = a small integer), e.g., the rubine dye, 2-bromo-4-nitroaniline  $\rightarrow$   $\alpha$ -(2-methoxy-5-methyl-*N*-2':3'-dihydroxypropylanilino)acet-*N*'*N*'-dimethylamide.<sup>97</sup> Dyes containing an *N*-allyl substituent are of the pattern: 5-nitro-2-aminobenzenesulphon-alkyl (or -hydroxyalkyl)amide  $\rightarrow$   $\text{NR}(\text{Aryl})\cdot\text{CH}_2\cdot\text{CHMe}$  (*R* = hydroxyalkyl or alkoxyalkyl).<sup>98</sup> Dyes containing carboxylic ester groups on an aliphatic side-chain are obtained from coupling components  $\text{NR}(\text{Aryl})\cdot\text{X}\cdot\text{CO}_2\text{Y}$  (*R* = H, alkyl or aryl, *X* = methylene or ethylene, *Y* = alkyl or aryl); e.g., the blue dye, 2-bromo-4-nitroaniline  $\rightarrow$  *N*-(5-hydroxy-1-naphthyl)-glycine methyl ester.<sup>99</sup> Dyes containing a ureido group on an aliphatic side-chain are obtained from coupling components:  $\text{NR}(\text{Aryl})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  (*R* = H or hydroxyalkyl).<sup>100</sup> Dyes are also prepared having a 4:5-dihydroxyamyl group in either the diazo or coupling component, the combination *p*-nitroaniline  $\rightarrow$  *o*-chloro-*N*-(4:5-dihydroxyamyl)aniline giving orange shades.<sup>101</sup>

The American Cyanamid Co.<sup>102</sup> use coupling components  $\text{NR}(\text{Aryl})\cdot[\text{CH}_2]_x\cdot[\text{O}\cdot\text{C}_2\text{H}_4]_y\cdot\text{OR}'$  (*R* = H, alkyl, hydroxyalkyl, etc., *R'* = alkyl; *x*, *y* = 1, 2, 3, or 4) to obtain dyes which will dye cellulose acetate rayon but are especially suited for dyeing fibres composed of vinyl chloride-vinyl acetate co-polymers in a dyebath containing a swelling agent<sup>103</sup>; e.g., the scarlet dye, *p*-nitroaniline  $\rightarrow$  *N*-ethyl-*N*-2-(2'-methoxyethoxy)ethylaniline. If a sulphonated diazo component is used, the resulting dyes can be used for wool.

The Eastman Kodak Co. have two specifications in which the arylamine coupling component contains a trifluoromethyl substituent. In the first,<sup>104</sup> the coupling component is a trifluoromethyl-aniline, -naphthylamine, -tetrahydroquinoline, or -benzomorpholine, and the derived dyes are exemplified by: 3:5-dinitro-2-aminobenzenesulphonyl-*N*-ethylamide  $\rightarrow$  2-methyl-7-trifluoromethyl-1-2':3'-dihydroxypropyl-1:2:3:4-tetrahydroquinoline which gives blue shades on Nylon. In the second,<sup>105</sup> the coupling component is a secondary or tertiary benzenoid amine having a trifluoroacetamido group in the *meta* position, the derived dyes being exemplified by: 6-chloro-2:4-dinitroaniline  $\rightarrow$  5-trifluoroacetamido-2-methoxy-*NN*-di-(2'-hydroxyethyl)aniline which gives greenish-blue shades on cellulose acetate rayon.

The Eastman Kodak Co.<sup>106</sup> couple the usual benzenoid amine coupling components with diazotised 5-nitro-2-aminobenzenesulphonyl-*N*-ethylamide to obtain dyes such as the pinkish-rubine of good light-fastness from *NN*-di-(2'-hydroxyethyl)aniline. Non-phototropic yellow to reddish-orange dyes are obtained by the Society of Chemical Industry in Basle<sup>107</sup> from diazotised 3:5-dinitroaniline and the usual amine

coupling components, *e.g.*, *NN*-di-(2-hydroxyethyl)aniline gives a reddish-orange dye.

In the field of blue dyes, British Celanese Ltd.<sup>108</sup> prepare dyes of the pattern: 6-nitro-2-aminobenzthiazole  $\rightarrow$  3-acetamido-*NN*-di-(2-hydroxyethyl)aniline (optionally substituted with, *e.g.*, alkoxy or halogen in position 6) which are bluer in shade than those they described earlier from other aminothiazoles.<sup>109</sup> Naphthylamines, particularly *N*-substituted derivatives of 1-amino-5-naphthol, continue to be popular as coupling components for blue shades. Using 1-2': 3'-dihydroxypropyl- (or -2'-methyl-2': 3'-dihydroxypropyl-)amino-5-naphthol as coupling component, the Eastman Kodak Co. obtain blue to bluish-green shades from the diazo components (*a*)<sup>110</sup> 5-nitro-2-aminobenzotrifluoride, (*b*)<sup>111</sup> 5-nitro-2-aminobenzenesulphon-alkyl- (or -dialkyl-)amide, and (*c*)<sup>112</sup> 5-nitro-2-aminophenyl alkyl sulphone.

The Eastman Kodak Co. have continued their investigation of heterocyclic coupling components most of which contain a N atom in the heterocyclic ring which directs coupling to the corresponding *para* position in a fused benzo ring. Thus, they use a lilolidine<sup>113</sup> derivative to obtain dyes such as the blue-green 3:5-dinitro-2-aminobenzene-sulphonyl-*N*-2'-hydroxyethylamide  $\rightarrow$  3:7-dihydroxy-3:7-dimethyl-lilolidine.<sup>114</sup> They also use a 1:2:3:4-tetrahydroquinazoline coupling component having an alkyl or hydroxyalkyl, etc., substituent on the 1-N atom.<sup>115</sup> A 1:2-dialkyl-1:2:3:4-tetrahydroquinoline or 3:4-dialkylbenzomorpholine is coupled with a diazotised 4-nitroaniline having H or nitro in position 2 and H or halogen in position 6,<sup>116</sup> or with a diazotised 5-nitro-2-aminobenzenesulphonalkylamide which may have nitro in position 3;<sup>117</sup> *e.g.*, there are obtained the dyes 2-chloro-4-nitroaniline  $\rightarrow$  2:7-dimethyl-1-2': 3'-dihydroxypropyl-1:2:3:4-tetrahydroquinoline (rubine), and 5-nitro-2-aminobenzenesulphonyl-*N*-2'-methoxyethylamide  $\rightarrow$  3:6-dimethyl-4-2'-hydroxypropylbenzomorpholine (violet).

In the field of water-soluble dyes of the general pattern, A  $\rightarrow$  E as defined above, Imperial Chemical Industries Ltd. have described an interesting series of dyes which show superior exhaustion on cellulose acetate rayon when dyed from the dilute liquors used in winch machines.<sup>118</sup> Thus they couple a diazotised *p*-nitroaniline (which may be substituted except with SO<sub>3</sub>H, CO<sub>2</sub>H, and CN) with the sulphuric ester of an *N*-hydroxyalkyl-*N*-phenyl- (or -naphthyl-)alkylaniline (alkyls of 2-4C),<sup>119</sup> and with the sulphuric ester of an *N*-hydroxyalkyl-*N*-phenoxy- (or -naphthoxy-)alkylaniline (alkyls of 2-5C),<sup>120</sup> either of which may have substituents (other than SO<sub>3</sub>H or CO<sub>2</sub>H) in the aryl nuclei. The dyes cover a range of shades depending on substitution and are exemplified by *p*-nitroaniline  $\rightarrow$  *N*-2-hydroxyethyl-*N*-2'-phenylethylaniline sulphuric ester (scarlet), and 2:6-dichloro-4-nitroaniline  $\rightarrow$  *N*-2-hydroxyethyl-*N*-2'-*p*-chlorophenoxyethylylaniline sulphuric ester (orange-brown). From 4-nitro-2-cyanoaniline (optionally substituted by halogen in position 6) as diazo component and coupling components of either of the above types they obtain reddish-violet to reddish-blue dyes, *e.g.*, 4-nitro-2-cyanoaniline  $\rightarrow$  *N*-2-hydroxyethyl-*N*-2'-phenylethyl-*m*-chloroaniline sulphuric ester (reddish-violet).<sup>121</sup> They also couple a

diazotised *p*-nitroaniline with the sulphuric ester of an *N*-alkyl-*N*-2-hydroxy-3-aryloxypropylaniline, aryl being phenyl (optionally substituted with chloro, alkyl, or alkoxy) or naphthyl.<sup>122</sup> and with the sulphuric ester of an *N*-hydroxyalkyldiphenylamine (alkyl of 2-3C).<sup>123</sup> The dyes obtained cover a range of shades and are exemplified by *p*-nitroaniline  $\rightarrow$  *N*-ethyl-*N*-2-hydroxy-3-phenoxypropylaniline sulphuric ester (red), and 2:6-dichloro-4-nitroaniline  $\rightarrow$  *N*-2-hydroxyethyl-diphenylamine sulphuric ester (orange-brown). Finally, they couple a diazotised 4-nitroaniline having halogen, nitro, or cyano in position 2, and H or halogen in position 6 with an *N*-(C<sub>5-6</sub>-)alkyl-*N*-hydroxy-(C<sub>2-5</sub>-)alkylaniline (the sum of the C atoms in the alkyl and hydroxyalkyl groups being not greater than 10) which may be substituted in the *meta* position with halogen, methyl, C<sub>1-4</sub>-alkoxy<sup>124</sup>; an example is 2-chloro-4-nitroaniline  $\rightarrow$  *N*-2-hydroxyethyl-*N*-*n*-hexylaniline sulphuric ester (crimson). In all cases, the final products may be obtained by the alternative procedure of sulphating the dye derived from the unsulphated coupling component. Yellow dyes having similar exhaustion properties have been described earlier in this review.<sup>90</sup>

The Society of Chemical Industry in Basle<sup>125</sup> prepare dyes, *p*-nitroaniline or unsulphonated substituted derivative  $\rightarrow$  a *para* coupling *NN*-di(hydroxyalkyl)aniline, in which the benzene ring may be substituted and the two alkyls may be different, which are converted into mixtures of the mono- and di-sulphuric esters containing not more than one mol. of diester to each mol. of monoester by the action of 1.0 to 1.5 mols. of a sulphating agent. The dyes may also be made by sulphating the coupling components prior to coupling. The mixtures are stated to have better affinity for cellulose acetate rayon than the diesters and better solubility than the monoesters, and are exemplified by 4-nitro-2-cyanoaniline  $\rightarrow$  sulphonation product of *NN*-di-(2-hydroxyethyl)-*m*-toluidine and substantially 1.3 mols. of chlorosulphonic acid (violet). The same firm prepare sulphuric ester dyes by nitrating in sulphuric acid medium (so effecting simultaneous nitration and sulphonation) dyes of the pattern: a *m*- or *p*-nitroaniline  $\rightarrow$  NR<sub>2</sub>Ar<sub>2</sub>·R'·OH, where R is H or alkyl and R' is alkylene<sup>126</sup>; e.g., *m*-nitroaniline  $\rightarrow$  *N*-2-hydroxyethyl-*N*-butylaniline is nitrated in concentrated sulphuric acid to give a reddish-brown water-soluble dye. They also prepare water-soluble dyes of the pattern, Ar·N<sub>2</sub>·Ar·NR·CO·X·CO<sub>2</sub>H, in which one of the aryl nuclei contains OH *ortho* to N<sub>2</sub>, the *tert.* N is *para* to N<sub>2</sub>, R is H or alkyl, and X is an organic residue containing at least one unsaturated linkage, and may be aromatic.<sup>127</sup> The dyes yield yellow to red shades on cellulose acetate rayon and nylon, and may also be used for wool and silk. For example, 4-amino-2'-hydroxy-3-methoxyazobenzene (by hydrolysis of *O*-*p*-toluenesulphonyl-*o*-aminophenol  $\rightarrow$  *o*-anisidine-*N*-methane- $\omega$ -sulphonic acid) is reacted with phthalic anhydride in chlorobenzene to give a water-soluble yellow dye.

Dyes especially suitable for dyeing polyamide fibres such as Nylon are metallisable or metal-containing monoazo dyes devoid of sulphonic acid groups; developments in this field in Germany were reviewed last year.<sup>128</sup> E. I. Du Pont de Nemours & Co.<sup>129</sup> dye Nylon with metal (preferably copper) complexes of water-insoluble monoazo compounds,

*e.g.*, the copper complex of 4-nitro-2-aminophenol  $\rightarrow$  1-phenyl-3-methyl-5-pyrazolone which gives golden-brown shades. They also prepare dyes suitable for dyeing Nylon (or wool) by an afterchrome or one-bath chrome process by coupling 2 : 7-dihydroxynaphthalene with a diazotised amine having in the *ortho* position OH, CO<sub>2</sub>H, O-CH<sub>2</sub>-CO<sub>2</sub>H, or S-CH<sub>2</sub>-CO<sub>2</sub>H, and devoid of sulphonic acid groups.<sup>130</sup>

A well established method of producing navy-blue to black shades on cellulose acetate rayon consists in applying thereto a diazotisable aminoazo compound followed by diazotisation on the fibre and coupling with a suitable coupling component, particularly 2-hydroxy-3-naphthoic acid. With this coupling component, the Eastman Kodak Co.<sup>131</sup> use a 2-fluoro-4-aminoazobenzene having NRR' (R, R' = alkyl or hydroxy-alkyl) in the 4'-position for navy-blue to black shades, *e.g.*, the product obtained by reducing the nitro group of 2-fluoro-4-nitroaniline  $\rightarrow$  *NN*-di-(2-hydroxyethyl)aniline. They also use a 4-aminoazobenzene having NRR'' in the 4'-position and SO<sub>2</sub>-NR'R''' in the 2-position (R, R' = H, alkyl, or hydroxyalkyl; R'', R''' = alkyl, hydroxyalkyl, or phenyl) for diazotisation and development on the fibre<sup>132</sup>; *e.g.*, 4-amino-4'-dimethylaminoazobenzene-2-sulphonyl-*N*-methylethylamide gives navy-blue to black shades with 2-hydroxy-3-naphthoic acid, and blue with 2-methyl-1-2' : 3'-dihydroxypropyl-1 : 2 : 3 : 4-tetrahydroquinoline. Manufactures de Produits Chimique du Nord Etablissements Kuhlmann<sup>133</sup> obtain green shades by diazotising on the fibre and developing with 2-hydroxy-3-naphthoic acid an azo compound of the pattern : primary arylamine devoid of SO<sub>3</sub>H or CO<sub>2</sub>H  $\rightarrow$  1-amino-2-naphthyl hydroxyalkyl ether. Francolor<sup>134</sup> use a 4 : 4'-diaminoazobenzene having an alkyl or alkoxy group in the 3- and optionally in the 2'-position for tetrazotisation and development on the fibre with 2-hydroxy-3-naphthoic acid to give fast violet to blue shades.

British Celanese Ltd.<sup>135</sup> obtain green shades fast to wet treatments, gas fumes, and light by diazotising on the fibre a 1-amino- (or 1-hydroxy-)4-aminoarylaminoanthraquinone (*e.g.*, 1-methylamino-4-4'-aminoanilinoanthraquinone) and developing with a phenylphenol or cyclohexylphenol (*o*-phenylphenol gives the most brilliant shades). When the anthraquinone nucleus contains a primary amino group, diazotisation is best effected in acetic acid medium which leaves this group undiazotised, since tetrazotisation which occurs in mineral acid medium gives rise to tertiary shades.

### Lakes and pigments

E. I. Du Pont de Nemours & Co. use 6-chloro-*o*-toluidine as a diazo component for coupling with 2-hydroxy-3-naphthoic acid to give a red pigment for use in coating compositions,<sup>136</sup> and they prepare its acetoacetyl derivative for use as a coupling component for pigments of the Hansa Yellow type.<sup>137</sup> They prepare metal complexes (especially nickel and copper) of azo compounds obtained by coupling a compound of the 4-hydroxypyridone series with a diazotised arylamine devoid of SO<sub>3</sub>H, CO<sub>2</sub>H, and of OH groups *ortho* to the amino, for use in printing inks, lacquers, etc.,<sup>138</sup> *e.g.*, the nickel complex of *o*-chloroaniline  $\rightarrow$  2 : 4-dihydroxyquinoline. Violet to brown pigments prepared by the

same firm are the copper, nickel, or cobalt complexes of dyes : arylamine-*o*-carboxylic acid  $\rightarrow$  a 2-hydroxy-3-naphthoic arylamide.<sup>139</sup>

Imperial Chemical Industries Ltd.<sup>140</sup> prepare brown pigments suitable for the mass pigmentation of viscose rayon by carrying out an azo coupling giving a yellow, orange, or red pigment in presence of carbon black.

The General Printing Ink Corp.<sup>141</sup> have found that, contrary to expectation, pure colours of high tinctorial value are obtained from tetrazotised mixed diaminodiphenyls (see page 74). The same firm obtain pigments of superior physical properties by adding simultaneously solutions of diazo and coupling component to a buffered aqueous liquid so that at any time the coupling component is in slight excess and the concentration of either component is low.<sup>142</sup> A method of making azo lakes of uniform physical properties described by E. I. Du Pont de Nemours & Co.<sup>143</sup> consists in diazotising the amine in presence of the coupling component and effecting coupling by making alkaline.

British Celanese Ltd. use dyes containing long chain aliphatic radicals for producing coloured cellulose acetate rayon by incorporating the dye in the spinning solution. Dyes containing two such radicals ( $C_8$  or more) preferably attached to the same atom have very high solubility in acetone.<sup>144</sup> Yellow-shade fibres are produced from monohydroxyazobenzenes containing in the nucleus carrying the OH a hydrocarbon radical ( $C_{12}$  or more),<sup>145</sup> e.g., aminoazobenzene  $\rightarrow$  oleylphenol, whilst red-shade fibres are obtained from monoazo dyes containing an oleoyl-amino radical in at least one of the components,<sup>146</sup> e.g., *p*-nitroaniline  $\rightarrow$  3-oleylamino-1-diethylaminobenzene.

A reddish-blue pigment for colouring cellulose acetate lacquers or spinning solutions, or nitrocellulose lacquers, obtained by the Society of Chemical Industry in Basle<sup>148</sup> is the chromium complex of 5-nitro-2-aminophenol  $\rightarrow$  4-benzoyl-1-naphthol.

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## ANTHRAQUINONE DYES (J. Wardleworth, M.Sc.)

### Acid wool dyes

LITTLE of outstanding novelty has appeared in this field during the period under review, new developments being confined mainly to extension of the use of derivatives of 1:4-diaminoanthraquinone substituted at positions 5, 6, 7, and 8.

Sandoz Ltd.<sup>1</sup> prepare fast reddish-blue dyes for wool and synthetic nitrogen-containing fibres by halogenation of 1-amino-4-2':6'-dialkyl-anilinoanthraquinone-2-sulphonic acids, optionally substituted in the 4'-position of the anilino group by alkyl or alkoxy. Condensation of 4-bromo-1-aminoanthraquinone-2-sulphonic acid or -carboxylic acid with 4-amino-4'-alkylsulphamylidiphenyls in presence of urea affords dyes of blue to green shades, fast to light and washing, for wool, nylon and related fibres.<sup>2</sup>

Blue dyes of improved shade-stability to artificial light derived from 4-halogeno-1-aminoanthraquinone-2:6- or -2:7-disulphonic acids are described by Sandoz Ltd. The first type<sup>3</sup> are reddish-blue, prepared from anilines substituted in the *meta* position by alkyl, carboxy, carbalkoxy or halogen, whilst greenish-blue dyes are obtained<sup>4</sup> by employing acylaminoanilines, optionally further substituted by alkyl, carbalkoxy or halogen. Use of a halogen-free hydroaromatic amine, bearing the amino group in the hydrogenated nucleus, *e.g.*, cyclohexylamine and its homologues or 2-amino-1:2:3:4-tetrahydronaphthalene, also affords bright blue dyes.<sup>5</sup>

Violet, blue or green dyes of high fastness are obtained by the same inventors,<sup>6</sup> from 6- and/or 7-halogenoanthraquinones carrying a group NH·CHXY (where X = aralkyl and Y = alkyl or aralkyl) in the 1- and/or 4-positions, by sulphonation; *e.g.*, the base from 6-chloroquinizarin and 1:3-diphenylisopropylamine affords a fast, pure blue dye. Similarly,<sup>9</sup> green dyes of outstanding shade in artificial light are obtained by sulphonation of 6:7-dihalogeno-1:4-diarylaminoanthraquinones, the anilino groups being the type usually employed for wool dyes.

E. I. Du Pont de Nemours & Co.<sup>7</sup> obtain dyes for cellulose acetate, fast to gas fumes, by condensing leuco-1:4:5-trihydroxyanthraquinone with aniline or its alkyl or hydroxyalkyl derivatives, followed by oxidation. The 4-arylamino-1:5-dihydroxyanthraquinones so obtained afford acid wool dyes on sulphonation.

The same company<sup>8</sup> prepare a fast blue, milling dye by sulphonation of 1 : 4-bis-(2' : 4' : 6'-triethylanilino)anthraquinone, obtained from 1 : 4-diaminoanthraquinone and 1-bromo-2 : 4 : 6-triethylbenzene. This is merely a variation on an old theme. Sulphonation of 1 : 4-diarylamino-anthraquinones carrying an acylamino group at position 5, and optionally further substituted at position 8, affords green dyes according to the Society of Chemical Industry in Basle.<sup>10</sup>

E. I. Du Pont de Nemours & Co.<sup>11</sup> find that sulphonation of 1-arylamino-6-(4'-aminoanthraquinonylamino)anthraquinones yields grey dyes, which are fairly stable to chroming.

### Dyes for cellulose esters

The recent patents are confined to the description of new blue dyes with improved fastness to gas-fume fading.

Eastman Kodak Co. obtain dispersed dyes<sup>12</sup> by esterification of both hydroxy groups of 1 : 4-di-(2'-hydroxyethylamino)anthraquinone with simple aliphatic acids, the ester groups being the same or different whilst condensation of 1 : 4-dihydroxy-, 1 : 4 : 5-trihydroxy- or 1 : 4 : 5 : 8-tetrahydroxy-anthraquinone with an amine of the type  $\text{NH}_2 \cdot \text{Q} \cdot \text{O} \cdot \text{R} \cdot [\text{OR}]_n \cdot \text{OR}'$  (where  $\cdot$  = *o*- or *p*-phenylene,  $\text{R} = [\text{CH}_2]_2, [\text{CH}_2]_3$  or  $\text{CH}_2 \cdot \text{CHMe}$ ,  $\text{R}' = \text{H, Me, or Et}$ , and  $n = 1$  or  $2$ ) affords dispersed reddish-blue dyes.<sup>13</sup>

British Celanese Ltd.<sup>14</sup> prepare 1-amino-3-cyanoanthraquinones carrying  $\text{CO}_2\text{H}$  or  $\text{SO}_3\text{H}$  at position 2 and a group  $\text{NHR}$  (where  $\text{R} = \text{alkyl, aryl, aralkyl or cycloalkyl}$ ) at position 4 by treating derivatives of 1 : 4-diaminoanthraquinone-2-carboxylic acid or -sulphonic acid with alkali metal cyanides under mild conditions. The products are fast-to-light, greenish-blue dyes.

Alkyl- and hydroxyalkyl-amides of 1-amino- or 1-alkylamino-4-halogenoanilinoanthraquinone-2-carboxylic acid, which have high resistance to gas-fume fading, are obtained according to the above firm,<sup>15</sup> either by condensation of the appropriate 4-halogenoanthraquinone with a halogenated aniline, or from 1 : 4-substituted anthraquinone-2-carbonyl chlorides and ammonia or aliphatic amines, e.g., 4-bromo-1-aminoanthraquinone-2-carbonyl-2'-hydroxyethylamide is condensed with *m*-chloroaniline, or 1-amino-4-*m*-chloroanilinoanthraquinone-2-carbonyl chloride is treated with monoethanolamine to give 1-amino-4-*m*-chloro-anilinoanthraquinone-2-carbonyl-2'-hydroxyethylamide.

### Vat dyes

No notable advances have been made in this field, but the use of alkyl- and aryl-sulphonyl groups, previously employed in dyes of the acylamino-anthraquinone series, to obtain certain effects or to increase fastness properties, has now been extended to dyes of the phthaloylacridone and carbazole types.

The Society of Chemical Industry in Basle<sup>17</sup> describe the preparation of further examples of anthraquinone amides, by interaction of anthraquinonedicarboxylic acids with vatable amines, which may contain heterocyclic rings. The major attention is devoted to amides from 1 : 5-diaminoanthraquinone-2 : 6-dicarboxylic acid which yields dyes

mainly of violet to red-brown shades with aminoanthraquinones carrying acylamino groups. Oxazoles, iminazoles and thiazoles are obtained by acylation of *o*-diamino-, *o*-aminohydroxy- and *o*-aminomercapto-anthraquinones.

The use of heterocyclic derivatives of anthraquinone-dicarboxylic acids for acylation of amines, at least one of which is vatable, originates from the same source.<sup>18</sup> Examples are mainly confined to the acylation of substituted aminoanthraquinones with anthra-1 : 9-5 : 10-dithiazole-2 : 6- and di-*N*-methylantra-1 : 9-5 : 10-dipyrazole-2 : 6-dicarboxylic acids which afford fast yellow to red shades.

Kuhlmann obtain a fast, reddish-brown dye<sup>19</sup> by condensation of 1 : 4-diaminoanthraquinone with 1-chloro- and 1 : 5-dichloro-anthraquinones to give an anthrimide, and subsequent ring-closure, and describe the production of a dye which yields olive shades on cotton, in contrast to the more usual yellow, by fusion of 1 : 1'-5 : 1'-trianthrimide with potash in ethanol; tinctorial power is improved by chlorination.<sup>20</sup>

New brown carbazole dyes are obtained according to the Society of Chemical Industry in Basle<sup>10</sup> by cyclisation of the trianthrimides prepared from 1 : 4-dihalogeno-5-acylaminoanthraquinones and amines, usually vatable, with agents such as aluminium chloride, titanium chloride, etc. The American Cyanamid Co.<sup>21</sup> claim improvement in yield and purity of the carbazoles obtained by use of the latter reagent, the bromide, and the corresponding zirconium compounds.

The Society of Chemical Industry in Basle<sup>22</sup> produce carbazoles of varying shade, suitable for printing a variety of textile materials and for conversion to leuco-ester salts, by cyclisation of 1 : 1'-dianthrimides containing -SOR or -SO<sub>2</sub>R groups, preferably in a pendant benzamido residue.

Two patents<sup>23, 24</sup> by General Aniline Co. describe carbazole dyes of the thiaxanthone series, analogous in type to those previously prepared from phthaloylacridones. Orange to brown shades are obtained by condensation of a 5-chloro-2 : 3-phthaloylthiaxanthone, prepared by condensing 2-chloroanthraquinone-3-carboxylic acid with a *m*-chlorothiophenol and subsequent cyclisation, with a 1-aminoanthraquinone, the product then being ring-closed to a carbazole. The second patent describes dyes in which the thiaxanthone and carbazole systems are linked by an amide bridge, prepared by condensing a 5-(*o*-halogenobenzamido)-1 : 2-phthaloylthiaxanthone with a 1-aminoanthraquinone.

Simple acylamino-phthaloylacridones are described in two patents by the Society of Chemical Industry in Basle.<sup>25, 26</sup> Dyes giving blue shades, stable to soaping, are obtained by acylation of 3-amino-1 : 2-phthaloylacridones, free from substituents at positions 6, 7, 8, and 9, with *p*-halogenobenzoic acids, whilst on acylation with cinnamic acid and its derivatives blue to green dyes are obtained. Bright greens are prepared by condensation of 3-amino-1 : 2-phthaloylacridone with 2-*p*-halogenobenzamidoanthraquinones.<sup>27</sup>

Imperial Chemical Industries Ltd. have two patents on 1 : 2-phthaloylacridones containing sulphone residues. 3-Acylamino derivatives of 1 : 2-phthaloylacridones, substituted in positions 6, 7, 8, or 9 by alkylsulphonyl, dye cotton in blue to violet shades,<sup>28</sup> whilst acylation of a

3-amino-1 : 2-phthaloylacidone, devoid of alkyl- or aryl-sulphonyl groups, with alkyl-, aralkyl- or aryl-sulphonylbenzoic acids also affords dyes of similar shade.<sup>29</sup> Both types have high light fastness.

The American Cyanamid Co.<sup>30,31</sup> prepare  $\alpha$ -acylamino derivatives of 1 : 2-6 : 7- and 1 : 2-8 : 9-diphthaloylacidones, which dye cellulosic fibres in orange to brown shades of improved brightness, by cyclisation of 1 : 1'- or 2 : 1'-dianthrimide-carboxylic acids, produced by condensation of (a) an "o"-halogenoanthraquinone-carboxylic ester or nitrile with an aminoanthraquinone or (b) an "o"-aminoanthraquinonecarboxylic ester with a chloroanthraquinone followed by hydrolysis, with acidic reagents.

Kuhlmann<sup>32</sup> prepare dyes of widely varying shade and high fastness by condensation of 3'-halogeno-2-alkyl- or 3'-halogeno-2-aryl-4 : 5-2' : 1'- or -4 : 5-1' : 2'-oxazoles or -iminazoles with vatable amines. Acylation of the products usually induces a marked change in shade.

R. H. L. Bretagne<sup>33</sup> describes the use of a new reagent, silver oxide, for the oxidation of leuco-2-aminoanthraquinone-9 : 10-disulphuric ester and its derivatives to indantrones; the silver formed is stated to be easily recoverable for re-use.

Purification of dialkoxydibenzanthrones, resulting in dyeings of brighter shade, is achieved according to Imperial Chemical Industries Ltd. by vatting the crude dye in aqueous caustic alkali solution of a heterocyclic nitrogenous base, *e.g.*, pyridine. Oxidation of the vat causes separation of the pure dye and impurities are removed in the filtrate.<sup>34</sup>

The same firm<sup>35</sup> describe the use of new catalysts, consisting of compounds of vanadium or molybdenum, for the amination of dibenzanthrone with hydroxylamine or its derivatives in sulphuric acid solution. These catalysts enable the reaction to be carried out at lower temperatures than hitherto, thus obviating sulphonation and producing grey to black dyes with improved fastness to wet treatments.

A notable advance has been made by the American Cyanamid Co.<sup>36</sup> in the preparation of sulphuric esters of vat dyes in aqueous media; previously this reaction has necessitated the use of anhydrous solvents. Esterification of the leuco compound, preformed in aqueous alkali, by reaction with sulpho compounds of tertiary amines having dissociation constants of  $10^{-7}$  or more at 25° avoids the difficulties associated with the use of anhydrous conditions, especially on the manufacturing scale.

### Oil Colourants

Red to violet dyes, soluble in mineral oils and petrol, are prepared according to American Cyanamid Co.<sup>37</sup> by condensing alkylamines, *e.g.*, butyl-, amyl- or hexyl-amine with 2-alkylantraquinones containing one or two  $\alpha$ -nitro groups, *e.g.*, 1-nitro, 1 : 5-dinitro- or 1 : 8-dinitro-2-methylantraquinone.

### Phthalocyanines

Phthalocyanine pigments, free from halogen, which maintain their tinctorial strength in contact with organic paint, lacquer or plastic

vehicles, are obtained, according to American Cyanamid Co.,<sup>38</sup> by transforming the finely divided, acid-pasted pigment to a coarse form by heat-treatment in air, water or an organic liquid, then grinding in presence of a grinding aid, *e.g.*, carbohydrates, silica, inorganic salts, etc., and finally stabilising the product by treatment with a crystallising solvent.

Sandoz Ltd.<sup>39</sup> describe the preparation of green metal-containing hexadecahalogenophthalocyanines by heating tetrahalogenophthalic acid derivatives with a heavy metal compound, and a catalyst consisting of a compound of an element of group V or VI in an inert high-boiling solvent.

Phthalocyanines on treatment with paraformaldehyde, 1 : 1'-dichloro- or 1 : 1'-dibromo-dimethyl ether and aluminium chloride, preferably in presence of a tertiary amine not susceptible to halogenomethylation, are found by Imperial Chemical Industries Ltd.<sup>40</sup> to give derivatives useful as intermediates. For example, blue to green water-soluble dyes for textiles are obtained from a phthalocyanine containing at least two halogenomethyl groups, by treatment with a tertiary amine or a derivative of thiourea, or by reaction with an alkali derivative of a thiol, and subsequent alkylation.<sup>41</sup> Reaction of chloromethylated copper phthalocyanine and *p*-nitrothiophenol, followed by reduction, affords an aminoaryl derivative.<sup>42</sup> The latter patent describes further examples of amino-arylphthalocyanines, giving diazo compounds which possess greater stability than those from nuclear aminophthalocyanines, in which the aminoaryl groups are linked to the phthalocyanine nucleus by S, SO<sub>2</sub>, SO<sub>2</sub>O, O, CO, CH<sub>2</sub>O, CH<sub>2</sub>, NR-SO<sub>2</sub>, NR-CO, NH or NR.

Blue and green sulphur dyes with improved wet fastness, patented by Imperial Chemical Industries Ltd.,<sup>43</sup> are made by interaction of metal-containing or metal-free phthalocyanines carrying at least one -SO<sub>2</sub>Cl group and phosphorus pentasulphide (or its constituent elements) in an inert solvent; *e.g.*, copper phthalocyanine-tetra-4-sulphonyl chloride affords a bright green cotton dye.

### Miscellaneous dyes

Kodak Ltd.<sup>44</sup> find that 2-nitrodiphenylamines containing a group -SO<sub>2</sub>NHR (where R = H, alkyl or NH<sub>2</sub>) in the same ring as the nitro group dye organic derivatives of cellulose, nylon, etc., in yellow shades and have better affinity than previously known dyes of the same type.

The Society of Chemical Industry in Basle<sup>45</sup> describe fast-to-light, greenish-yellow, dispersed dyes of improved affinity for organic derivatives of cellulose, obtained by condensation of *p*-mono- or *p*-di-alkylamino-benzaldehydes with hydroxyalkyl esters of cyanoacetic acid.

A further type of nitro dye, also dispersible, with good affinity for cellulose esters and ethers, and free from the defect of sublimation, is obtained according to Kuhlmann<sup>46</sup> by condensation of 1-halogeno-2-nitro-4-sulphonamides or -sulphonyl chlorides with ammonia, primary or secondary amines.

Imperial Chemical Industries Ltd.<sup>47</sup> produce dispersible yellow dyes for cellulose derivatives, polyamide and polyester fibres, of outstanding light fastness, by reaction of oxindole or its simple derivatives with a

*p*-diethylaminobenzaldehyde substituted in the 2-positions of the ethyl groups by  $-\text{CN}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{CO}_2\text{R}$  or halogen.

Solvent-soluble dyes suitable for use in cellulose ester spinning solutions, of the azo, anthraquinone and nitrodiarylamine series, containing two alkyl groups in the range octyl and octadecyl are patented by H. C. Olpin, K. R. House and J. Wright.<sup>48</sup>

Fluorescent dyes for nitrogenous fibres such as wool and silk are obtained, according to American Cyanamid Co.<sup>49</sup> by sulphonation of hydroxyalkylaminophthalimides.

The Society of Chemical Industry in Basle<sup>50</sup> have discovered that the use of mixtures of 4- and 6-chloro- (or -bromo-) 3-hydroxy-7-methylthionaphthenes in the preparation of thioindigoid dyes has no adverse effect on their properties. The derived dyes are as fast and pure in shade as those obtained by using the pure 6-chloro compound and superior to those from the pure 4-chloro isomer.

Pennsylvania Bituminous Coal Research Inc.<sup>51</sup> prepare brown dyes of good fastness, for wool, silk and synthetic fibres, by treating a bituminous coal or lignite with nitric acid, and extracting the resulting dye with an organic acid or aqueous alkali.

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# IRON AND STEEL

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STEEL output in 1948 attained an all-time record of 14,877,000 tons. This must be attributed, in part, to expansion already carried out in accordance with the industry's development plan of 1946, designed to increase steel plant capacity to 16 million tons by 1952 or 1953. Other important contributory factors to this achievement include the excellent response to the home scrap drive, the adoption of a continuous working week in the steel plants, and the increased application of oil-firing, which accelerates melting and, in consequence, increases output. Pig iron and ferro-alloy production in 1948 was 9,290,000 tons of which 7,020,000 tons pig iron was utilised for steel making.

According to the latest estimates of the British Iron and Steel Federation it is apparent that the originally estimated demand of 16 million tons of steel for 1953 is inadequate. Since 1946, both home and export demands have increased and a more appropriate target would now appear to be 18 million tons. The flexibility of the original plan should enable the increased steel plant capacity to be achieved without difficulty, but concern is felt regarding the supply of raw materials.

## Mineral resources and treatment of iron ores

A large number of surveys of mineral resources have recently been prepared. Whilst the scope of many of these is purely parochial, and the surveys therefore of limited interest, others have reviewed the world situation with respect to mineral supplies. Amongst these latter may be mentioned Durrer's<sup>1</sup> review of manganese resources, whilst molybdenum and vanadium resources have been assessed by Charrin<sup>2</sup> and chromium resources by Demassieux.<sup>3</sup> Of great interest and importance is the discovery in Quebec and Labrador of large deposits of rich iron ore. According to Campbell,<sup>4</sup> 300 million tons of ore containing about 60% iron are already proven and there is evidence of much larger quantities of somewhat leaner ores, containing 40-50% iron.

Research, with the object of improving sinter quality, has continued. McLeod,<sup>5</sup> continuing the investigations of Hay and McLeod mentioned in the 1947 report, notes the beneficial effect of lime additions to iron ore sinters. Since the poor reducibility of sinters is attributable to the coating of iron oxide with impervious silicate slag, improvement in reducibility may be achieved by addition of lime which displaces ferrous oxide from the silicate, and so raises the melting point of the slag, which is then less liable to close the micro-pores of the sinter. The extent of the improvement in reducibility is indicated by the fact that the addition of 10% of lime to sinter charges halves the time required for 90% reduction.

In Sweden, Jansson and Danielsson<sup>6</sup> have investigated the effects of

sintering under increased vacuum, in a Greenawalt plant at Domnarfvet, using three different degrees of vacuum, 2200 kg./m<sup>2</sup> (3.13 lb./in.<sup>2</sup>), 1500 kg./m<sup>2</sup> (2.13 lb./in.<sup>2</sup>) and 1000 kg./m<sup>2</sup> (1.42 lb./in.<sup>2</sup>). With other conditions maintained constant, it was found that the sintering rate increased with the square root of the vacuum, whilst power consumption was directly proportional to the vacuum. Sinter quality was unaffected and there was no appreciable change in the relative resistance of the charge to air passage.

In England, attention has been directed to the problems of iron ore beneficiation; in particular, the United Steel Companies have installed a special ore-dressing laboratory, and at the Appleby-Frodingham and Workington branches, research is being carried out at the pilot plant stage. At Appleby-Frodingham, Reeve<sup>7</sup> describes experiments with a pilot plant for the magnetic roasting of lean ores. The roasting is carried out in a cylindrical rotating kiln, 23 ft. in length by 1 ft. 10 in. internal diameter, fired with blast furnace gas to a temperature of 700–790° C. After roasting, the ore is magnetically separated. Results with the lean Frodingham calcareous ores are very encouraging, giving an increase in iron content from between 22 and 24% to between 36 and 38%, with an iron recovery of the order of 90%, the iron content of the tailings being only about 6%. The efficiency of magnetic concentration, as distinct from enrichment arising merely from the loss of volatile constituents, is measured by the concentration factor:

$$\frac{\% \text{ Fe in concentrate (calcined)}}{\% \text{ Fe in original ore (calcined)}} \times x \% \text{ Fe recovery,}$$

which takes into account only the enrichment resulting from the elimination of slag-forming constituents and gives equal prominence to concentration and iron recovery. With the Frodingham ores, concentration factors between 115 and 120 are obtained. Preliminary experiments on Northamptonshire siliceous ores have not been so encouraging, the chemical combination of the principal slag-forming constituents with iron, in the form of an iron-aluminium-silicate known as chamosite, making physical separation less satisfactory.

At Workington, where hematite iron is smelted from relatively rich ores, there is still a considerable concentration problem involving particularly the elimination of barytes, which occurs to a considerable extent in some of the local hematite deposits. Research is proceeding on flotation methods for barytes elimination. The ore-preparation plant recently installed at Workington<sup>8</sup> consists of a crushing and screening plant and a Greenawalt sinter plant.

The work proceeding in the new ore-dressing research laboratory<sup>9</sup> includes investigation of methods of crushing, milling, grinding and screening of ores and research on various methods of ore beneficiation, including those involving flotation and magnetic roasting.

The theory and practice of crushing iron ore are comprehensively discussed by Howat.<sup>10</sup>

### Production of pig-iron

Extensive research, with the object of increasing efficiency of pig-iron production, is being undertaken by the Iron Making Division of the

British Iron and Steel Research Association in collaboration with the industry and with other research organisations, notably the British Cast Iron Research Association and the British Refractories Research Association. Towards the end of 1947 a summary of the work in progress was published by Bishop.<sup>11</sup>

More recently, general trends in pig-iron manufacture have been considered by Colclough and Scott-Maxwell,<sup>12</sup> who emphasise particularly the importance of burden preparation and coke quality. With respect to the former, grading, screening and classification of ores used is considered to be essential and it is stressed that all fines, below 0.5 in. mesh, should be removed and sintered. Where the ores used are of very diverse qualities, they should be put through a suitable bedding plant to give a more uniform burden. It is considered that the desired quality of blast furnace coke should be more readily obtained if the ovens were under the control of the iron maker. All coke should be crushed, screened and classified, and the small coke rejected and used for other purposes. As possible methods of increasing production and improving efficiency in the future, the use of high top-pressure and oxygen enrichment of the blast are suggested. A third possibility is the application of compensated charging as described by Saunders and Wild.<sup>13</sup> This is a device for the improvement of stock distribution by replacing the usual bell and hopper with a charging gear which permits of charging material either towards the centre of the stack or towards the walls. Although a suitable design for the large scale application of such a device has not yet been developed, it is likely that much smoother working would result from the improved stock distribution.

Oxygen enriched blast and high top-pressure operation are still being investigated as means of increasing efficiency. After an outline of the history of the use of oxygen in the blast furnace, Howat<sup>14</sup> concludes that real advantages are offered by oxygen enrichment but that the limit for practical operation seems to be of the order of 25-30% oxygen by volume. In any case, the use of oxygen enrichment will necessitate considerable modification in design and operation. The quantitative aspects of oxygen are considered in some detail by Rocca and Bever,<sup>15</sup> who also conclude that the optimum concentration of oxygen in the blast is about 30%. Large-scale experiments with oxygen-enriched blast have been carried out in France at Neuves-Maisons, where an enriched-air production unit has been installed to give 3500 cu.m. (124,000 cu.ft.) of enriched air (48% oxygen) per hour. These experiments, including the use of both oxygen-enriched blast and fuel oil injection are described and discussed by Platon.<sup>16</sup>

The American work on high pressure operation is reviewed by Revie,<sup>17</sup> and the engineering aspects of the subject are considered by Old, Pepper and Poor.<sup>18</sup> The necessary modification to existing plant apart from alterations and additions to the blowing equipment should not be expensive.

Encouraged by the success of acid-smelting at Corby, experiments on similar lines have been conducted at various works in France, including Caen, Senelle, Denain and Neuves-Maisons. According to Chenet,<sup>19</sup> however, nowhere was the anticipated improvement achieved, and it is

concluded that closer control of the operating variables is required before success can be expected.

The incidence of blast-furnace scaffolds has been reported by Chesters, Halliday, and Mackenzie,<sup>20</sup> who have examined a number of scaffolds *in situ* and have also investigated the behaviour of scaffold-forming materials in the laboratory. Examination of the scaffolds showed them to consist of displaced brickwork behind which carbon deposition had occurred and on the face of which there were accretions of fused or partially fused burden agglomerates. The displaced brickwork itself was rich in potassium-aluminium silicates indicative of alkali attack. It was not possible to assess the extent to which alkali attack had contributed to scaffold formation, but certainly it would tend to promote adhesion of the burden. The laboratory investigation showed that, although all the iron ores examined softened and adhered to fireclay bricks, when heated to temperatures below the melting point of the ore, no similar adhesion occurred with carbon bricks. It was further shown that, whilst carbon bricks burnt quite rapidly in  $\text{CO}_2$  at  $1000\text{--}1200^\circ\text{C}$ ., the rate of combustion decreased very rapidly with either decrease in temperature or introduction of carbon monoxide or nitrogen. The possibility is now being investigated of reducing scaffold formation by lining the central portion of the stack with carbon bricks, though it is possible that improved burden preparation and distribution might well reduce the tendency to scaffold formation.

Carbon refractories are in fact finding increasing favour for both blast furnace hearths and linings; progress in this field is reviewed by Debenham.<sup>21</sup> The question of blast-furnace design in general has been critically reviewed by Hogberg<sup>22</sup> who, from a study of the effect of various design variables upon performance, concludes that the provision of adequate volume in the lower zone of the furnace is of utmost importance. An appendix including parts and dimensions of a blast-furnace is included with the object of helping to standardise nomenclature.

An interesting item of design is the "double auger tuyère" described by Sprow,<sup>23</sup> which, by means of vanes set in the tuyère nose, imparts a twist of  $90^\circ$  to the blast. It is claimed that, using such a tuyère, the blast penetrates further into the furnace, and as a result more coke is burnt with the same amount of blast; coke consumption per ton of iron produced is decreased without detriment to iron quality.

There have again been a number of physico-chemical investigations of the iron-making processes. The effects of operating conditions upon the type of reduction occurring and upon coke consumption have been studied by Taylor,<sup>24</sup> who shows that, other conditions being similar, efficiency of operation increases with increased indirect reduction, rather than with direct reduction. Coke-rate should, therefore, be adjusted to give a minimum value for the  $\text{CO}/\text{CO}_2$  ratio in the top-gas, corresponding to conditions of maximum indirect reduction. The maximum indirect reduction attainable varies with slag bulk, blast temperature, radiation losses and moisture in the burden.

Elimination of sulphur in the blast-furnace is discussed by Joyce.<sup>25</sup> An obvious preliminary is to charge as little sulphur as possible and, since in general more than 90% of the sulphur charged comes from the

coke, the use of coke of low sulphur content is particularly important. Removal of the sulphur unavoidably charged is effected by appropriate slag control, and for this a slag of adequate basicity is essential. If the slag is too lean, the fusion zone is extended and heat concentration is insufficient either to heat the iron or to effect desulphurisation and the resulting iron is of low temperature and high sulphur content. On the other hand, the slag should not be so basic that the temperature required to flux it is higher than that of the hearth, as this leads to derangement of furnace operation by deposition of unfluxed lime in the hearth. The use of oxygen as a means of rapidly controlling hearth conditions, is viewed as a future possibility. Alternatively, rapid slag control might be facilitated by the introduction of flux through the tuyères. This would permit of the use of a low melting point slag in the bosh, giving maximum furnace driving rate, with an enriched slag in the hearth for sulphur removal. The amount of limestone which need be charged would incidentally be reduced, making available more heat in the shaft and increasing the reducing power of the gases. The provision of adequate hearth heat, during the injection period, is a problem requiring solution before such a method could be operated successfully.

Hydrogen has distinct advantages as a reducing agent for iron ores; the weight of hydrogen required to reduce a given weight of iron ore is much less than the corresponding weight of carbon, and reduction with hydrogen is more exothermic than either direct or indirect carbon reduction. Discussing this, Platon<sup>26</sup> admits that for many years it is improbable that hydrogen will be available at a price which would permit its economic use in the blast-furnace. The use of hydrocarbons, however, may not be impossible and Platon's calculations show that, if a hydrocarbon containing 15% of hydrogen and 85% of carbon were injected into a blast furnace, 1 cwt. of fuel oil should replace 1.6 cwt. of coke and half the contained hydrogen should be recovered in the gas with resulting enrichment. There are obstacles to successful fuel oil injection, but it has already been found possible to inject 2-4 cwt. of fuel oil or pulverised coal per ton of iron, with corresponding saving in coke.

### Foundry practice

The year's progress in one aspect of foundry practice, grey-iron production, is surveyed by Schaum,<sup>27</sup> who considers at some length the highlights of development in this field.

The main research and development work on cupola practice has concerned the possibility of using oxygen-enriched blast. From a number of reports of successful experimental runs in U.S.A., with oxygen-enriched blast, the following advantages are evident: (i) melting rate is increased, (ii) with the same iron/coke ratio, metal temperature is increased, or, alternatively, similar operating conditions may be maintained with decreased coke consumption, (iii) loss of metalloids by oxidation is decreased. If oxygen-enrichment results in much higher operating temperatures, lining life must inevitably suffer; according to Wick,<sup>28</sup> however, increased refractory wear may be avoided by suitable oxygen manipulation. There does not appear to be complete agreement as to the limits of enrichment which may usefully be employed; Gregg,<sup>29</sup>

for instance, suggests that more than 10% enrichment appears to have detrimental effects; whilst Higgins<sup>30</sup> discusses the advantages of up to 25% enrichment. Both Wick and Higgins consider the possible merits of the intermittent use of oxygen for special purposes, *i.e.*, to remove bridging and other operating difficulties, or to produce hot iron at short notice. Higgins particularly recommends the use of oxygen to accelerate the melting of the first charge of the day.

An alternative method of obtaining benefits, similar to oxygen-enrichment, is to use heated blast. Methods suggested by Healy<sup>31</sup> for obtaining the hot blast include: (a) the use of heat exchangers burning either the waste gases or external fuel, and (b) utilisation of the sensible heat of the gases in the stack by circulating the air for combustion around the cupola shell.

Another line of cupola development is the application of induction heating, as designed by Piowowsky.<sup>32</sup> After preliminary laboratory investigations, Piowowsky constructed a cupola combining the use of coke and induction heating—the hearth of the cupola being induction heated with the object of superheating the metal to the extent of 100–200° c. Energy consumption was only about 60–120 kw. hr./ton.

At the steel foundry of Catton and Co. Ltd., Leeds, the use of oxygen enrichment, in the side-blown converter, has been developed to such a stage that it is now incorporated in normal practice. Advantages accruing from the use of 30–35% oxygen blast, as described by Harrison, Newell, and Hartley,<sup>33</sup> include the production of steel of higher temperature and consequently increased fluidity, shorter blowing time and, therefore, increased output, and decreased blowing loss. It is interesting to note also that the end-point was easier to control and a more consistent final product obtained using oxygen-enrichment. Since oxygen-enrichment of the converter blast allows molten iron of lower temperature to be used, there is some resultant fuel economy in the cupola, which is also able to utilise more scrap, with a saving in pig-iron consumption. Another saving is in the amount of ferro-silicon required during cupola melting and subsequent blowing in the converter.

The occurrence of “peel” in whiteheart malleable castings, reached serious proportions during the war, and extensive research work was carried out to investigate its causes and means of elimination. Much of this work is published by the Iron and Steel Institute as a symposium. After an introduction by Humfrey,<sup>34</sup> various other authors record the results of their investigations. “Peel” may occur during the malleablising of whiteheart cast iron as a result of iron sulphide deposition below the metal surface. In association with some inter-crystalline oxidation, a surface layer is produced which is easily detached from the main body of the casting. The primary cause of “peeling” is the use of high sulphur ores for malleablising, whereby an atmosphere of high sulphur content is obtained around the casting. In gas malleablising, “peeling” does not occur because the composition of the atmosphere is controlled and the dangerous high sulphur contents can be avoided. There is some difference of opinion regarding the effect of state of oxidation of the ore upon peel formation. On the one hand, Preece and Irvine<sup>35</sup> show that sulphur penetration occurs only in the presence of a relatively reducing atmosphere

of high  $\text{CO}/\text{CO}_2$  ratio, and conclude, therefore, that "peeling" may be obviated by using an ore of sufficiently high ferric oxide content to ensure relatively oxidising conditions. On the other hand, Webster and Probst<sup>36</sup> report rather more pronounced "peeling" when using highly oxidising ores than occurred with less oxidising ores. This conclusion is confirmed also by the British Cast Iron Research Association investigations, described by Bernstein.<sup>37</sup> In his introduction, Humfrey suggests that the two views are not entirely incompatible if the mechanism is as indicated by the work of Preece and Irvine, namely that for sulphur penetration a reducing atmosphere of high carbon monoxide content is essential, but that segregation of the sulphide to form a subcutaneous layer can proceed only after decarburization to a suitable depth by means of an oxidising atmosphere. "Peel" formation will result, therefore, if the ore used is initially sufficiently oxidising to cause decarburization but gradually weakens during the process, until conditions become sufficiently reducing to permit sulphur penetration from an ore of appreciable sulphur content.

Enumerating desirable properties of the metal for the avoidance of "peel" formation, Bowden<sup>38</sup> in the same symposium, specifies a sulphur content as low as possible and silicon as low as is consistent with ready response to malleablising, the manganese content should be relatively high, up to about 0.4%.

### Production of steel

The essential design of steel-making furnaces has undergone no radical change, but increasing attention is being given to various items of construction, with a view to improving efficiency of operation.

Of the standard open hearth furnace designs, the Venturi type has some claims to superiority. Its characteristics are discussed by Smoliarenko and Efanov,<sup>39</sup> whilst Lane<sup>40</sup> considers its particular merits for oil-firing and utilisation of oxygen, for both combustion and bath injection. After being in disfavour for a number of years, the Terni furnace is reconsidered by Ferri,<sup>41</sup> who claims that the accelerated melting rates and economic fuel consumption, which can be achieved in this type of furnace, with the improved refractories, now available, offer considerable advantage.

The potential advantages of an all basic construction for open hearth furnaces were appreciated before the war, but could not be realised during the war, because of shortage of suitable raw materials. Although the cost of refractories for a chrome-magnesite roof is about four times that for a silica roof, there is reason to believe that the benefits of longer roof-life and increased production rates, resulting from higher but safe roof temperatures would more than justify the extra cost. With some improvement in the supply position, the project is now being resumed and Pluck,<sup>42</sup> towards the end of 1947, discussed the principles upon which it was proposed to construct an all-basic furnace at the Templeboro works of Steel, Peech, and Tozer Ltd.

An experimental open hearth furnace at the Shelton Iron, Steel and Coal works is being used by the British Iron and Steel Research Association for the study of combustion problems, and a description of the

plant, by Leckie, Hall, and Cartlidge,<sup>43</sup> was published last year. The furnace is a small-scale replica of one of the existing furnaces at Shelton; it is fired with mixed blast furnace and coke oven gases but the design is simplified by operating as a one-way furnace without pre-heat. It was decided that more accurate combustion data could be obtained if the furnace were operated below steel-making temperatures, using calorimeters for the determination of the rate of heat-flow to the hearth. The first experimental results, in which various operating and constructional factors are considered, are described by Leckie, Allen, and Fenton.<sup>44</sup> It was found that the best results were obtained using theoretical air/gas ratio, with a gas of high calorific value and a high furnace pressure. Ports should be designed to give rapid mixing of gas and air and from subsequent experiments on various modifications of the Maerz port, Allen, Cook, and Fenton<sup>45</sup> guardedly conclude that this type of port appears to give slightly better results than the ordinary port.

Perspex models designed for the study of simulated air and gas flow, in the open hearth furnace, are described by Phillip.<sup>46,47</sup> Flow in the models was at first recorded by photographing streams of suspended aluminium particles in water passing through the model. Later it was found that very turbulent flows could be studied photographically by introducing a stream of gas to the water and illuminating with a discharge tube.

Increasing appreciation of the importance of instrumentation has led to the formation, by the British Iron and Steel Research Association, of an Open-Hearth Instruments Sub-Committee. As a contribution to the work of this Committee, Rogers<sup>48</sup> has surveyed the problems involved and the first report of the Sub-Committee, presented by Robertson,<sup>49</sup> includes a list of suggested instruments for both gas and oil-fired furnaces, together with recommended procedures for their use.

Although instrumentation, for measurement and recording of operation variables in iron and steel works practice, is well established, direct automatic control is very much in its infancy. For the guidance of the industry, Thompson<sup>50</sup> has prepared a survey of electronic and servo-electronic devices and their application to the automatic control of iron and steel works processes.

The acceleration of melting achieved in the open hearth furnace by oxygen enrichment, emphasises the shortcoming of open hearth charging, and Harry<sup>51</sup> has considered the engineering aspects of accelerating charging. Amongst other considerations, the suggestion is made that the size of the furnace doors should be increased, so that the capacity of the charging pans also might be increased. The logical conclusion of this suggestion is Longenecker's<sup>52</sup> proposal to use a furnace with an "all door" front. His design was inspired by the successful operation of "all door" front reheating furnaces.

The use of oxygen in steel-making, both open hearth and Bessemer, has been further developed during the year, and American progress in the open hearth applications has been very fully reported. The only British experience so far published concerns the side-blown converter

(see p. 108), and although intensive research on other applications is proceeding in several British steel-works, these investigations are not yet sufficiently advanced for publication.

Adequate control of slag composition during refining is of supreme importance in basic open-hearth steel-making and much work has been devoted to improvements of methods for achieving this control. A series of articles by Funk,<sup>53</sup> on the functions of basic open-hearth slags and on the various methods available for their control, helps considerably to clarify the position. In a paper given to the Cleveland Institution of Engineers by Kesterton,<sup>54</sup> the application of general methods of slag control to the specific problem of rimming steel production is discussed, and stress is laid on the need for a slag of adequate iron oxide content to ensure good rimming action and of composition to give appropriate sulphur and phosphorus removal.

All slag control methods depend upon a knowledge of slag basicity, which must be determined so that the required additions may then be assessed. Of the established methods for determining slag basicity, usually expressed as the V-ratio,  $\text{CaO}/(\text{SiO}_2 + \text{P}_2\text{O}_5)$ , chemical analysis and visual examination of slag pancakes are commonly employed. The chemical methods, though accurate, are generally less speedy than is desirable, whilst the evaluation of slag pancakes, although rapid, is not sufficiently accurate. Seeking a method combining speed and accuracy, Philbrook, Jolly, and Henry<sup>55</sup> found an empirical correlation between the basicity of a slag and the  $p_{\text{H}}$  of its water extract. Smith, Monaghan, and Hay,<sup>56</sup> investigated further the possibilities of the  $p_{\text{H}}$  method, and found it incapable of giving the V-ratio with sufficient accuracy; they then developed a similar method based upon the conductivity of the water extract instead of upon its  $p_{\text{H}}$ . It is claimed that by this method, the V-ratio can be determined to the required accuracy in about 20 minutes, provided the slag is homogeneous and free from undissolved lime, the presence of which can completely invalidate the method.

An interesting fundamental study of the rate of sulphur migration across a slag-metal interface is reported by Chang and Goldman.<sup>57</sup> Using melts of Armco iron, with synthetic slags and admixed ferrous sulphide, it was shown that, whilst the coefficient,  $K_s$ , of transfer of sulphur from slag to metal is not materially affected by slag composition, the coefficient,  $K_m$ , of transfer from metal to slag increases rapidly with increasing slag basicity. Temperature changes also have a greater effect on  $K_m$ , which is increased by about 12% for a rise in temperature of  $10^\circ \text{C}$ ., than upon  $K_s$ , with an increase of only 6% for the same temperature increase.

Constant attempts are made to produce cleaner steel with superior mechanical properties by improved de-oxidation technique. An interesting method of open-hearth de-oxidation is described by Chuprin.<sup>58</sup> Fine coke is spread evenly over the surface of the bath at the conclusion of refining and de-oxidation proceeds by diffusion of carbon into the bath. It is claimed that the steel produced has better mechanical properties than normally de-oxidised steel, and that sulphur and phosphorus contents are not adversely affected. Yield from manganese and silicon additions also is materially improved.

De-oxidation is probably effected most efficiently by using carbon under vacuum. Thomas and Moreau<sup>59</sup> carried out laboratory experiments in a small high frequency furnace and showed that in vacuum, the reactions between carbon in the steel and oxide inclusions were promoted, until, with the pressure reduced to 0.01 mm. of mercury, a steel was obtained containing only 0.002% oxygen and 0.007% carbon. According to Colombier,<sup>60</sup> pressures low enough to degas molten steel thoroughly cannot be obtained on the industrial scale because of the large volumes of gases absorbed in the refractories. Useful deoxidation may, however, be effected at somewhat higher pressures applicable to several tons of steel.

The degassing, by vacuum heating, of ferro-alloys for special steel production has been investigated by Hochmann.<sup>61</sup> Hydrogen, nitrogen, and carbon monoxide were substantially removed from most metals by heating *in vacuo* at temperatures between 600 and 1400° c. Of the metals investigated only aluminium did not respond to this treatment.

From a study of the incidence of hydrogen in steel and its removal therefrom, Sims<sup>62</sup> concludes that removal of hydrogen from an open hearth bath requires a very vigorous boil. Alternatively, as described by Hulme,<sup>63</sup> hydrogen may be removed by flushing with an inert gas such as nitrogen or argon. Useful elimination of solid inclusions is also effected by this means.

In a general investigation of the physical chemistry of iron- and steel-making processes, Oelsen<sup>64</sup> gives some attention to gases in steel. He quotes Naeser's observations regarding the absorption, by molten iron, of nitrogen from a mixture of gases; if the nitrogen is mixed with an oxidising gas, *e.g.* oxygen or carbon dioxide, no nitrogen is absorbed by the metal, but in the presence of a reducing gas, *e.g.*, carbon monoxide or hydrogen, the nitrogen is rapidly absorbed. In order, therefore, to obtain Bessemer steel of minimum nitrogen content, the blast should still be oxidising when it leaves the metal.

The improvements recently achieved at Corby in basic Bessemer steel quality are described by Dickie.<sup>65</sup> The aim was to produce basic Bessemer steel more free from the tendency to work-hardening and strain-age embrittlement, which arises principally from the high phosphorus and nitrogen contents. The problem, then, was to reduce the contents of these two elements in basic Bessemer steel. The phosphorus content was at first reduced by a double blowing process. After blowing in the normal manner, the slag was removed and more lime added prior to a second short blow of half a minute duration. In this way phosphorus was reduced to 0.025%, instead of the normal value of 0.050–0.055% in Bessemer steel, but there was no improvement in the nitrogen content.

Dickie discusses various methods by which nitrogen may be removed from Bessemer steel or fixed in an innocuous condition by suitable additions. However, prevention of absorption of nitrogen was considered preferable to any of the other alternatives, and to this end, the factors affecting nitrogen absorption were studied. It was established that the amount of nitrogen absorbed was related to five factors, (a) partial pressure of nitrogen (P), (b) the time of contact (t), (c) absolute temperature (T), (d) the surface area of contact between gas and metal (A), (e) the coefficient of diffusion (D), which is the percentage nitrogen

absorbed at standard temperature,  $T_s$ , when  $p = 1$ ,  $t = 1$ ,  $A = 1$ , according to the following expression :

$$Q = D \left( \frac{T}{T_s} \right)^5 p^{\frac{1}{2}} t^{\frac{1}{2}} A.$$

Beneficial decrease in pressure and time of contact may be effected concurrently by decreasing the bath-depth. A decrease in the partial pressure of nitrogen in contact with the charge is effected by additions of iron oxide ; oxygen-enrichment of the blast would be similarly beneficial. Somewhat paradoxically, the addition of oxide (mill scale is most suitable) slows down the rate at which the iron content of the slag increases, so that after blowing to the normal 0.05% phosphorus, the bath is not sufficiently oxidising to promote a good rimming action. The blow must, therefore, be continued for a short time to give the necessary state of oxidation, during which time the phosphorus content falls to about 0.03%. There is practically no nitrogen pick-up at this stage and the finished steel, as well as being low in phosphorus, has a low nitrogen content of the order of 0.008–0.010%. The new procedure gives steel of greatly improved physical and chemical properties.

To provide further information on the solidification and structure of steel ingots, Macnair<sup>66</sup> has prepared a series of ten ingots, ranging from wild to fully killed, from the same cast, by suitable additions of aluminium and iron oxide to the moulds. To explain the various structures obtained, Macnair uses the two fundamental principles of selective freezing and rate of reaction between free oxide and carbon. Whilst neither of these concepts is new, the investigation is of interest in that so wide a range of ingot types is considered, and further work is continuing.

The effect of gases on ingot solidification has been studied by Polin.<sup>67</sup> The investigation was carried out by first de-gassing steel melts under vacuum, and then saturating with the appropriate gas. Of the gases studied, hydrogen had the greatest effect on solidification ; steel free of hydrogen, did not, under any conditions develop dendritic crystals, there being a definite range of hydrogen contents within which dendritic structures occur.

Acceleration of gas-evolution during teeming, by mechanically shaking the ingot mould, is described by Geigel.<sup>68</sup> The shaker device may be used to assist difficult rimming action and an improved yield is obtained on rolling as a result of the more solid ingots produced.

Rolling yield from killed steel is improved by electrical hot-topping to reduce piping, as described by Kopecki.<sup>69</sup> The top of the ingot is maintained molten by a submerged electrode. Power consumption is about 20 kw. hr. per ton of ingots.

## Properties

Towards the end of 1947, the Institute of Metals, in association with other interested societies, held an important symposium on internal stresses in metals and alloys. Although all the papers included provide valuable information on some aspect of the subject, it is not possible here to consider each individually. Brief mention, however, might be made of some of the papers of more chemical interest. Andrew and Lee,<sup>70</sup>

studying the relationship between cold work and hydrogen absorption, show that cold work increases the capacity for hydrogen absorption, presumably because it increases irregularity and discontinuities in crystal structure where hydrogen occlusion can occur. The calculated pressure of the occluded hydrogen is 8.6 tons per sq. in. The use of X-rays for measuring lattice strain is considered by Wood,<sup>71</sup> and a review of internal stresses arising from transformations has been prepared by Thompson.<sup>72</sup> The effect of internal stresses on corrosion resistance is dealt with by Evans.<sup>73</sup> Investigating the behaviour of oxide films when removed from the parent metal, Evans observed that thick films wrinkle and thin films crack and curl into rolls. This behaviour is attributed to distortion of the oxide structure resulting from the increase in volume that occurs on oxidation; another factor is inheritance of stress gradients from the parent metal. Stress corrosion cracking in the presence of sulphur gases is reported by Rees,<sup>74</sup> who finds that although 18/8 stainless-steels suffer seriously from stress corrosion in the presence of moist  $H_2S$ , the effect is much less severe if the  $H_2S$  is dried.

Matthaes,<sup>75</sup> also studying stress corrosion, concludes that there is in general no minimum stress below which stress corrosion ceases to occur. In normal practice, however, the life is long enough at low stresses to give a reasonable safety factor. A suggested mechanism of stress corrosion cracking has been propounded by Waber and McDonald<sup>76</sup>; the application of mechanical stresses accelerates the precipitation of a new phase from the original supersaturated solution. The resulting two phases form a galvanic cell, so that the new phase is progressively attacked by the corrosive medium, as it is formed at the grain boundaries, and inter-crystalline fissure results. Cracking can thus be caused by the presence of dissolved nitrogen, free to form iron nitride; if the nitrogen is removed, or innocuously fixed by a suitable addition, the susceptibility to cracking is reduced.

The increasing incidence of hydrogen embrittlement with cold working, as already mentioned, has also been studied by Zapffe and Haslem.<sup>77</sup> Considering this phenomenon with specific reference to wire, these investigators point out that rough handling of coils of wire in the mill may cause sufficient cold work to render the wire susceptible to hydrogen embrittlement in subsequent pickling operations. Susceptibility to hydrogen embrittlement is at a minimum in the annealed condition and at a maximum in the hardened condition, increasing with cold work as noted. Increasing carbon content favours embrittlement. With stainless steel, embrittlement is generally more serious as a result of cathodic pickling than acid pickling. All acids investigated, with the exception of nitric acid, caused a similar degree of embrittlement.

Rosenfeld,<sup>78</sup> investigating the possibility of minimising embrittlement by addition of suitable inhibitors to the pickling acid, found that the addition of formaldehyde to a sulphuric acid pickle solution enabled the resulting embrittlement after pickling to be removed by a subsequent treatment in boiling water. With hydrochloric acid, an addition of quinoline formaldehyde or *p*-toluidine formaldehyde enabled embrittlement to be avoided without the necessity even of subsequent boiling with water.

Although nitrogen has little effect upon the hardenability of boron-free steel, it has been shown by Digges and Reinhart<sup>79</sup> that high contents of nitrogen render boron additions largely ineffective for improved hardenability. This deleterious effect may be obviated in high nitrogen material by additions of titanium or zirconium. Pumphrey and Jones<sup>80</sup> have developed an interesting correlation between hardenability and iso-thermal transformation data. For three steels considered, the hardenability curves along a Jominy bar, calculated from iso-thermal transformation data were found to be in good agreement with the results obtained experimentally.

The improvement in fatigue strength to be obtained from alloy addition has been studied by Epremian and Nippes.<sup>81</sup> The relative order of efficiency was found to be Ti, Mo, Si, Mn, Ni, Co, and Cr, which is in the inverse order of their solid solubility in iron.

In a preliminary investigation of small sulphur inclusions in steel, Colombier<sup>82</sup> added iron sulphide to one ingot of a chromium-molybdenum-nickel steel and left another untreated. The sulphur contents were 0.012 and 0.007% respectively. Tensile-strength and elongation were not effected by the sulphur addition but impact strength was perceptibly lowered. The types of inclusions occurring in the sulphur treated steel and another one containing 0.014% sulphur are described in a later paper.<sup>83</sup>

A comprehensive investigation of the effect of beryllium additions, up to 1.5%, on the properties of a series of steels of increasing carbon contents (0.05–1.0%) is reported by Aichholzer.<sup>84</sup> The  $A_{c1}$  point is slightly elevated with increasing contents of beryllium. In the unhardened state, beryllium confers considerably greater hardness, though the difference becomes less marked as the carbon content increases. Some improvement in resistance to scaling also results from additions of beryllium.

In a very interesting study of the composition of carbides in steel and their effect on properties, Austin<sup>85</sup> gives extensive evidence for the occurrence of various compositions of cementite. It appears that the carbon content of cementite in equilibrium with ferrite is substantially constant at the theoretical figure, but, when in equilibrium with austenite, the carbon content of the cementite decreases with increasing temperature. It is also shown that some of the carbon in cementite can be replaced by nitrogen or by alloying elements such as manganese, chromium, molybdenum, tungsten and vanadium, particularly the first two. At any given temperature the amount of alloying element in the carbide increases proportionately with the total content of the element in the steel.

### Heat-treatment and metallography

A reference index of recently published information on heat treatment, covering the heat treatment of steel, cast iron and non-ferrous alloys, has been prepared by Morrel.<sup>86</sup>

Investigating the decarburization of malleable iron during annealing, Schwartz and Hedberg<sup>87</sup> note that substantial decarburization of white iron occurs even above the  $A_3$  point of silico-ferrite. Grain boundary inclusions are found only in the presence of silicon and, for that reason,

they are assumed to be of silicate composition. The oxidation, accompanied by decarburisation, which occurs during the reheating and rolling of steel has been studied by Wallquist,<sup>88</sup> who, after a review of the literature and description of laboratory investigations, gives a report of the results obtained in full-scale experiments. Both laboratory and full-scale tests indicate that the primary factors governing oxidation and decarburisation are the time and temperature of reheating; gas composition and velocity have only a limited effect. The extent of decarburisation during reheating and rolling of billets was found to be materially reduced by prior grinding of the billets.

It has been demonstrated by Eilender and Mintrop<sup>89</sup> that the temperature of the pearlite-austenite transformation depends upon the rate of heating, a considerable elevation of the transformation point being evident at rapid rates of heating. In induction hardening, therefore, where the rate of heating is very rapid, the hardening temperature may be appreciably raised. The application of time-temperature-transformation curves, to determine the suitability of various steels for induction heat-treatment, is discussed by Boyer.<sup>90</sup>

The use of low temperature treatment of steel for increasing hardness and for structural and dimensional stabilisation has been widely acclaimed and much investigatory work carried out. At room temperatures, steels do not achieve maximum hardness and, moreover, transformation may continue for several years, causing changes of dimensions that may make the material unsuitable for high precision use. Treatment of the steel, after hardening, at sub-zero temperatures of the order of  $-120^{\circ}\text{F.}$  is claimed to improve the hardness and to render the steel structurally stable. A particular application is to the improvement of tool performance and Svahn<sup>91</sup> mentions average figures of 20 to 30% improvement achieved by low temperature treatment, whilst improvements of as much as 400% have been claimed in the United States. According to Boyer,<sup>92</sup> the efficacy of low temperature treatment is impaired if there is a long interval between hardening and subsequent refrigeration, or if the material is tempered prior to refrigeration. Thurlby<sup>93</sup> is of the opinion that many of the claims for sub-zero treatment are exaggerated, but admits the benefits which may be obtained in the case of high-speed steels. Selby and Rowland,<sup>94</sup> expressing a similar opinion, state that most of the improvements resulting from sub-zero treatment are given equally well by double quenching. Low temperature treatment appears to be justified only when it is important to avoid the distortion caused by double quenching.

The Hatfield Memorial Lecture, this year given by Professor Mehl,<sup>95</sup> was devoted to a consideration of the decomposition of austenite by a process of nucleation and growth. Howard and Cohen,<sup>96</sup> in a quantitative study of the transformation of austenite to martensite, have provided detailed data for the lower part of the austenite transformation-diagram.

The formation of sigma phase in 18/8 steels, containing molybdenum, and titanium or columbium, has been demonstrated by Kirkby and Morley,<sup>97</sup> and also by Smith and Bowen.<sup>98</sup> The sigma phase, which is hard, brittle, and non-magnetic, and is described by Smith and Bowen

as being analogous to the compound ferro-chromium, occurs when the steel is reheated in the range 500–970° c., particularly at 850° c. The presence of sigma phase in the steel is accompanied by increased hardness, with decreased ductility and loss of magnetism and, under certain circumstances, decreased corrosion resistance.

Blanter<sup>99</sup> has developed the technique of microscopical examination, so that accurate quantitative determinations may be made of the phases present in an alloy, and statistical treatment of measurements from a large number of fields give results agreeing closely with those of chemical analysis. Blanter<sup>100</sup> describes also a method for the investigation of rapid iso-thermal transformations. Using very thin samples, 0.1–0.2 mm. thick, and an electron tube-controlled electromagnetic device, the time required to attain temperature is only 0.035–0.06 seconds.

The use of micro-radiography for the examination of segregates and inclusions in steel is described by Betteridge and Sharpe.<sup>101</sup> A selective absorption method, with suitable choice of radiation, reveals not only segregates but also the distribution of the constituents within the segregates. In general, however, it is not possible to identify non-metallic inclusions. Thermodynamic calculations have been applied by Rollason and Bishop<sup>102</sup> to the estimation of types and amounts of inclusions in weld metal. The only data required are the FeO content of the slag and the total manganese and silicon contents of the weld metal. The total oxygen content of the metal is obtained by reference to a calculated relationship with the slag (FeO). Knowing the total manganese, silicon and oxygen contents of the metal, the inclusion composition can be determined and the content estimated with the aid of the FeO–MnO–SiO<sub>2</sub> equilibrium diagram.

Morrogh and Williams<sup>103</sup> have shown that nodular graphite structures may be produced, without heat treatment, in grey cast-irons, with marked improvement in mechanical properties. Addition of cerium to hyper-eutectic nickel-iron-carbon alloys, even those of low nickel contents, give a nodular structure on solidification, similar treatment of hypo-eutectic alloys is only partially successful. There is at present insufficient information to indicate the precise mechanism by which the cerium promotes the spherulitic crystallisation that undoubtedly occurs, but as cerium is a good desulphuriser and strong carbide stabiliser, one of its functions is doubtless to reduce the sulphur content of the iron to a low value essential to the production of a nodular structure. The new procedure is justifiably claimed by the authors to open a new field of cast-irons with a nodular structure in the "as-cast" state, since hitherto such a structure could be produced only by the rather lengthy malleablising process.

In an investigation of the carbides present in iron-carbon-silicon alloys, Marles<sup>104</sup> pays particular attention to a carbide phase which, unlike cementite, does not respond to heat-tinting. This phase occurs in alloys containing more than 2.5% silicon, the proportion increasing with increasing silicon content, until with 7% silicon all cementite has disappeared and the entire carbide phase is nonheat-tinting. The new phase, which it is suggested, may be an iron-silicon-carbide is less stable at elevated temperatures than cementite.

## Analysis

Examination of the literature shows that more attention has been devoted recently to the development of spectrographic methods than to any other single principle of analytical procedure; speed in operation making them particularly adaptable to iron and steel works control.

There was much useful discussion of the general application of spectrographic methods to metallurgical analysis at a Congress held in France by the Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques. Of the papers presented at this Congress, particular attention should be drawn to the detailed survey by Jean<sup>105</sup> of methods of spectrochemical evaluation. Also of interest is the report by Pheline and Castro<sup>106</sup> on the determination of very small amounts of boron by a spectrographic method, capable of giving results to an accuracy of 3% over the range 0.0006–0.019% boron.

Argyle and Price<sup>107</sup> have developed a simple nomographical method for the spectrographic evaluation of minor constituents, which is independent of gamma variation both across individual plates, and from one plate to another; the necessity for repeated standardisation is thus obviated.

Errors in spectrographic analysis of low alloy steels are the subject of a statistical study by Shirley, Elliott and Meeds,<sup>108</sup> according to whom the three main sources of variability are excitation response, small-scale plate variability and microphotometry. Variability in excitation response was found to be reduced by using silver or graphite auxiliary electrodes rather than two pencil electrodes from the steel sample. In the determination of chromium, under the most favourable conditions, total variability from all three sources corresponded to a standard deviation of about 2% for a chromium content of 0.77%. This degree of reproducibility is not so good as that reported by Vincent and Sawyer<sup>109</sup> in a paper extensively quoted in the present investigation. Their figure of only 0.7% variability, for a chromium content of 1%, is attributed, by Shirley and his co-workers, largely to the very small photometry error in the American work.

Investigating the effect of the size and shape of the specimen upon the results of spectrographic analysis, Koritskii and Edneral<sup>110</sup> report that considerable systematic errors may occur when the size of the plane exposed to the spark is smaller than the natural "spark stain." The size of the spark stain depends, among other things, upon the type of steel, and varies between 9 mm. in diameter for low alloy steels to 12 mm. for stainless steel. The mass of the specimen also is important and considerable errors occur in the analytical results if it is reduced below a certain limiting value, depending upon the thermal properties of the metal.

Of the elements normally occurring in steel, carbon is one of the most difficult to determine spectrographically, but several authors have recently reported the development of satisfactory techniques. Blank and Sventitsky<sup>111</sup> describe two spark methods, one depending on the double carbon line at 4267Å and the other using the C III line at 2296.9Å in the ultra-violet region. Both methods give a single straight line calibration

curve applicable to both iron and steel. A similar method also using the carbon line at 2296.9A is described by Garton.<sup>112</sup> Blank and Sventitsky claimed satisfactory results down to 0.1% carbon but Garton found difficulty in estimating less than 0.2% carbon because of interference from atmospheric carbon dioxide. Garton comments also on the possibility of obtaining different values for the carbon content of a given sample, depending upon whether it is in the quenched or annealed condition.

The use of spectrographic methods for slag analysis, particularly for the rapid estimation of slag basicity from the lime and silica contents, has been the subject of much development work. Steinberg and Belic<sup>113</sup> claim that the lime : silica ration of an open hearth slag may be determined with an accuracy of 10% in 15-20 minutes by a method using low-induction condensed spark. The successful operation of similar methods in Russia is described by Shisterman and Ustalova,<sup>114</sup> whilst Buyanov<sup>115</sup> describes an arc method for the complete analysis of slags in 20-25 minutes.

The time required for spectrochemical analysis may be reduced to a fraction of that formerly required if a direct reading instrument is used. In such an instrument, as described by Walters,<sup>116</sup> a line of the element to be determined is projected on to a photo-electric cell, a reference line is projected on to another photo-electric cell and the intensity of the required line determined by balancing one cell against the other. In this way ferrous metals may be completely analysed in less than a minute.

Of methods for the determination of small amounts of carbon in steel, the low pressure combustion method is among the more successful. Naughton and Uhlig<sup>117</sup> describe a modification of this method in which, after combustion of the carbon to CO<sub>2</sub>, the gas is collected in a liquid nitrogen trap and its pressure measured at known volume. This method is claimed to be more reliable than the standard combustion method. A method of determining the state of occurrence of carbon in steel is described by Klyachko and Shapiro.<sup>118</sup> After separating electrolytically carbon and carbides from the steel by anodic solution, the free carbon is separated from the carbide by flotation in an aqueous solution of potassium and mercuric iodide, of density between that of free carbon and the carbides.

Research on the occurrence and determination of gases in steel continues and Pigott<sup>119</sup> has extensively reviewed the field of occurrence, effects and determination of hydrogen, oxygen, and nitrogen in iron and steel. Nash and Baxter,<sup>120</sup> studying methods for the liberation of gases from iron and steel, find none of the existing procedures entirely satisfactory but conclude that the best results are obtained by solution in aqueous mercuric chloride solution under carefully controlled conditions. Even with this method, the presence of large amounts of carbon is not conducive to success. Comparing the gas content of terrestrial and meteoric steel, Nash and Baxter find essential similarity between the two.

On behalf of the Gases in Liquid Steel Study Group of B.I.S.R.A., Speight<sup>121</sup> discusses the aluminium bomb method for determining the oxygen content of liquid steel in acid and basic open hearth practice.

The method depends upon a determination of the alumina formed by aluminium treatment *in situ* of a bath sample taken in a special bomb-shaped mould; for this purpose both gravimetric and nephelometric methods have been studied, and the results compared with those obtained by vacuum fusion. Gravimetric estimation gives satisfactory results, whilst the nephelometric results are slightly less reproducible, probably because of different characteristics in the various absorptimeters used by the collaborating laboratories. The applicability of the aluminium bomb method to the determination of oxygen in de-oxidised metal baths was confirmed. A new vacuum fusion equipment, the Cenco-Derge apparatus, which is capable of giving the oxygen content of a chill-cast sample of steel in less than 20 minutes is described by Richards.<sup>122</sup>

A spectrographic method for determining oxygen is described by Castro and Pheline.<sup>123</sup> An aluminium killed sample of the steel is dissolved in acid and the residue fused with ammonium bisulphate. After addition of a known quantity of cobalt sulphate, the mixture is dissolved and a few drops of the solution dried on a copper electrode. A comparison of the relative intensities of the aluminium and cobalt lines in the spectrum, resulting from spark excitation, enables a quantitative determination of the alumina to be made.

Though the determination of hydrogen in solid steel by the vacuum heating method is well established, its determination in liquid steel is not so straightforward, because of the difficulty of sampling so that the hydrogen present in the liquid steel is retained on solidification of the sample. Two types of sample with this objective have been investigated by Speight and Cook,<sup>124</sup> namely (a) a sealed mould sample, which ensures the retention in the mould of hydrogen liberated from the specimen during solidification, and (b) a chilled pencil sample which aims at solidifying the sample so rapidly that the hydrogen is retained in the solid. It is concluded that the sealed mould provides a very satisfactory method of sampling, and that the chilled pencil method also has distinct possibilities, especially for rapid combined determination of oxygen and hydrogen. An alternative proposal for sampling steel without loss of hydrogen is made by Chuiko,<sup>125</sup> who suggests that metal should be withdrawn direct from the bath into a sampler under vacuum.

### Corrosion and protective coatings

Fontana,<sup>126</sup> in a concise survey of metallic corrosion, and means by which it may be controlled, enumerates eight types of corrosion, namely uniform attack, intergranular corrosion, pitting, dezincification, erosion-corrosion, galvanic corrosion, stress corrosion and concentration cell corrosion. Whilst admitting that such a classification is somewhat arbitrary with often close inter-relation between the various types, it is claimed that practically every case of corrosion failure comes under one or other of the eight categories.

The atmosphere is the most universal corrosive medium and much work is constantly devoted to the prevention and control of atmospheric attack. Dearden,<sup>127</sup> interested in this subject from the view-point of steel rails, has attempted a quantitative correlation of corrosion with

the prevailing climatic conditions, particularly rainfall. No such direct correlation was evident however, only 35–40% of the total corrosion occurring during periods of measurable rainfall. A further 35–40% may be attributed to the effects of humidity, whilst the remainder of the corrosion must have occurred during periods of drizzle and dew and drying after rain. Laboratory tests to confirm the effect of humidity showed marked increase in corrosion rate when the relative humidity exceeded 80%. An interesting feature of the field tests was the annual rust shedding that was observed; by February or March a maximum rust thickness of between 0.06 and 0.09 g./sq. cm. was attained, the majority of which regularly flaked off during June or July, leaving a thickness of only 0.03–0.04 g./sq. cm.

Since highly alloyed steels are precluded by their price from general constructional use, their resistance to atmospheric corrosion is not usually considered. However, to fill a gap in the existing knowledge of the effects of alloy additions and to provide information for the occasional structural applications of stainless steel in a decorative capacity, Shirley and Truman<sup>128</sup> have studied the behaviour of a series of highly alloyed steels in an industrial atmosphere. Two steels in particular gave outstandingly good resistance, one containing 18% chromium, 8% nickel and 2½% molybdenum and the other 24% chromium, 12% nickel and 3% tungsten, both of which suffered a corrosion loss only one thousandth that of mild steel. Studying the atmospheric corrosion of iron and steel wires, Hudson<sup>129</sup> stresses that the use, where practicable, of low alloy steel, instead of mild steel, for wires subject to atmospheric exposure, would result in considerable material and cost economy.

In a method, described by Preston,<sup>130</sup> for the accelerated measurement of resistance to atmospheric corrosion, industrial atmospheric conditions are simulated by a controlled warm humid atmosphere containing sulphur dioxide.

Chemical engineering constructional materials are frequently required to give resistance to strong acid attack, a condition that may often be met by the use of stainless steel. Snair<sup>131</sup> reports that good resistance to all concentrations of nitric acid is provided by both straight-chromium and chromium-nickel stainless steels, and that no advantage in this respect results from additions of molybdenum. For welding, however, niobium-bearing steel should be used. Stainless steels also give satisfactory resistance to mixtures of nitric acid with sulphuric, phosphoric or acetic acid, but no steel is sufficiently resistant when hydrochloric or hydrofluoric acid is mixed with the nitric acid. The resistance to attack by boiling nitric acid of sensitised stainless steels of three types, namely titanium-bearing, niobium-bearing and straight 18/8, has been studied by Stewart,<sup>132</sup> who reports that in all cases the rate of corrosion decreased as the acid concentration was decreased from 65 to 35%. At high nitric acid concentrations the niobium-bearing steels were much superior to the straight 18/8, which in turn were superior to the titanium-bearing steels. At lower concentrations, the difference in resistance decreased, until with 35% nitric acid, the three types gave almost identical resistance. The resistance of the straight 18/8 steels decreased as the carbon content increased from 0.05–0.13%, but was in all cases superior

to that of the titanium-bearing steels, in which the ratio of titanium to carbon had little effect.

From a study of the effect of boiling nitric acid on a variety of sensitised austenitic stainless steels, Pray<sup>133</sup> concludes that susceptibility to intergranular corrosion is due to precipitation of carbides at the primary grain boundaries. With compositions giving ferrite in the austenite matrix, however, the carbides precipitate in the ferrite, rather than at the grain boundaries, and intergranular corrosion is reduced or even completely suppressed. This method of eliminating intergranular corrosion is applicable to cast material only, since the presence of ferrite has serious deleterious effects on rolling and forging properties. In view of the low resistance of steel stabilised with titanium, Stewart (*loc. cit.*) does not agree that the intergranular corrosion of sensitised stainless steel can be attributed entirely to carbide precipitation.

The generally accepted theory that passivity results from the formation of an inert surface film of oxide, has resulted in many investigations of such films, both *in situ* and after removal from the parent metal. Mahla and Nielsen<sup>134</sup> isolated passive films from various ferritic and austenitic stainless steels using a bromine-methanol solution. These films, formed on initially pickled and film-free surfaces by exposure to the air or by passivation in nitric acid or nitric acid-potassium dichromate solutions, were very thin and contained chromic oxide and ferric oxide as major constituents.

Measurements, by Hackerman and Marshall,<sup>135</sup> show that the covering of chromium surfaces by a passive film has an appreciable effect upon their electrode potentials, even when the film is not thick enough to be detected by electron diffraction. According to Guitton,<sup>136</sup> passivation of stainless steel in aerated acid was considerably facilitated by a prior "sensitising" treatment in a solution of nitric acid (10% by volume) and sodium fluoride (2% by weight) at a temperature below 60° c.

Misch and McDonald<sup>137</sup> distinguish three different types of inhibitors, *viz.* surface conversion, adsorption and diffusion inhibitors. For the adsorption type of inhibitor, it is shown that there is a critical minimum concentration required to maintain a monatomic adsorbed layer—the use of a concentration slightly in excess of this is the most economical. A general review of the use of inhibitors for corrosion control is given by Hackerman.<sup>138</sup>

During the war, the production of tinplate by electrolytic processes began substantially to replace the old hot dipping process, because of the need for tin economy, and shortly after the war the installation of such a plant<sup>139</sup> was commenced by Richard Thomas and Baldwins Ltd. at Ebbw Vale. The plant which is of Ferrostan type started production in April 1947 and is giving very good service. Much of the work of a new laboratory<sup>140</sup> installed by the British Iron and Steel Research Association at Sketty Hall, Swansea, concerns the South Wales tinplate industry.

Clauser<sup>141</sup> describes a method, the Protectatin process, for protecting tinplate by the formation of a thin oxide film. Dipping the tinplate into a hot alkaline phosphate-chromate solution containing a wetting agent produces an oxide film, which affords protection against sulphur-staining and rusting in moist air. Similar methods for the protection

of zinc coatings by anodically or chemically converting the surface to oxide or chromate were discussed by Stareck and Cibulskis<sup>142</sup> at the 1947 Annual Convention of the American Electroplaters' Society.

The relative merits of nickel and chromium for electro-deposition are discussed by Wilson.<sup>143</sup> For resistance to fretting corrosion and corrosion fatigue, nickel is superior to chromium, but chromium is much harder than nickel and preferable as a bearing material because of its smoother surface.

The Marine Corrosion Sub-Committee of the British Iron and Steel Research Association has devoted much attention to a study of compositions for the prevention of settlement and growth of plant and animal forms on ship bottoms and other steel structures immersed in sea water. The fundamental requirement of such anti-fouling compositions is their ability to release contained toxic material to sea water. This property, for a series of anti-fouling compositions, has been investigated by Barnes,<sup>144</sup> either cuprous or mercuric oxide being used as the poisonous pigment. A secondary inert pigment is required in association with the poisonous pigment and, for this purpose, red iron oxide was almost exclusively used. The vehicle for the pigments consisted of a component susceptible to attack, usually rosin, together with a resistant second component, or binder, for which Bedesol stand oil, in the form of a varnish, was found most suitable.

The use of cementiferous paints, originally suggested by Evans in 1940, has been developed by the B.I.S.R.A. Corrosion Committee as described by Mayne and Thornhill.<sup>145</sup> Essentially cementiferous paints are prepared by mixing zinc dust with certain chloride solutions, barium and strontium chlorides being most suitable, to give a matrix of oxy-chloride cement. Sufficient metallic zinc remains to provide cathodic protection to any steel surface remaining exposed at gaps and pores in the coating. The specific problem of applying cementiferous paints to the protection of steel from marine conditions has been studied by Pyefinch.<sup>146</sup> It is shown that, whilst the use of cementiferous paints for both priming and anti-fouling coats is not practicable, because of the gradual disintegration of the cementiferous matrix in sea water, they may be successfully used as primers if covered with an oleo-resinous sealing coat before the application of an oleo-resinous anti-fouling coat.

As part of the Corrosion Committee's work on protective coatings, Hudson and Banfield<sup>147</sup> report on the effect of atmospheric exposure on various non-metallic coatings applied to mild steel. The importance of surface preparation before painting was very evident, protective paint on a pickled surface being in good condition after five years exposure, whereas on a surface prepared only by weathering and wire brushing, failure occurred within  $1\frac{1}{2}$  years. Of other types of coating investigated by Hudson and Banfield, hot sprayed paints, in a stand-oil/wax medium containing no volatile matter, gave good service in an industrial atmosphere; a tar-tallow-lime mixture gave protection for three years, which is comparable with the life of a single paint coat of about the same weight; cement-asbestos coatings sprayed to a thickness of  $\frac{1}{4}$  in. gave good protection and vitreous enamel coatings were still perfect after five years exposure to either industrial or non-industrial atmospheres,

or two years immersion in sea water. Rubber-wax sheathing gave good protection against industrial atmospheres but was less satisfactory for marine atmospheres and sprayed bituminous coatings gave reasonably good results for sea water immersion.

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# NON-FERROUS METALS

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IT does not appear that any outstanding innovations in the practice of non-ferrous metallurgy have to be recorded as having been introduced during the year. An important symposium on the physical chemistry of reduction processes was organised by the Faraday Society, but, unfortunately, the record of the proceedings has not yet been published. In theoretical metallurgy, the 1948 American Institute of Metals Division Lecture, delivered by Dr. Cyril Smith, Director of the Institute for the Study of Metals at the University of Chicago, has drawn attention to the influence which surface tension forces may exert on the process of solidification of a metal and on the shape of metal crystals produced not only by solidification but also by recrystallisation and grain growth. There is evidence that this paper may have a notable influence on metallurgical thought.

## Mineral dressing

A feature of recent publications on froth flotation practice is the attention which has been given to the study of the behaviour of the particles while in the flotation machine. Fahrenwald<sup>1</sup> has pointed out that the impeller type of flotation machine acts both as an aerator and as a pulp pump. During aeration the air is compressed, the degree of compression varying with impeller depth. The effect of cell depth on the separation of quartz and magnesite was investigated, using an experimental cell of constant volume. The oleic acid collector was added in five portions, the concentrate being removed after each addition. Initial recovery and mineral recovery per unit of power was best with shallow cells, but total recovery was about 73% for all depths. The actual process by which mineral particles attach themselves to the air bubbles has been followed by Spedden and Hannan<sup>2</sup> by high-speed photomicrography. It was established that the attachment of the conditioned mineral to an air bubble takes place in less than 0.0003 seconds, but it was not possible to obtain precise details of how an air-mineral interface is formed. Collector-coated mineral particles can and do attach themselves to free air bubbles; fine particles are influenced by the flow of fluid around the bubble surface to a greater extent than coarser particles, and bubbles released from an orifice are not spherical and exhibit a distinct oscillatory motion.

A new type of sink-and-float concentrator—the selective media concentrator—has been described by H. L. McNeill.<sup>3</sup> This uses a suspension of a fraction (the “selective fraction”) of the ore instead of the usual heavy medium and treats ores which are difficult to de-slime or which contain coarse silica particles. The pulp, which should contain 40% of solids, is fed into a hollow inverted cone containing an inverted

conical impeller, with an ascending current of water. The heavy particles are impelled against the stationary cone and settle out; this crowds the lighter particles into the rising current near the impeller, which lifts them to the tailing discharge. A useful discussion has also been published of the theory and use of continuous and automatic centrifuges for classifying and de-watering aqueous and non-aqueous slurries and pulps in which the particles range in size from 150 to  $0.25\ \mu$ . These machines are now in service for such applications as the classification of pigments and cement slurries, the closed-circuit grinding and classification of ores prior to flotation, the cleaning of foundry sand, and the de-watering of coal fines, bauxite-muds, and many inorganic salts.

Details have been reported of several specific concentration schemes. Kennedy and O'Meara,<sup>4</sup> of the United States Bureau of Mines, studied the flotation of beryllium ores and found that beryl-bearing pegmatites and a helvite-bearing tactite could be satisfactorily treated for the recovery of the beryllium mineral by flotation with oleic acid and pine oil, preferably after a preliminary scrubbing treatment with alkali or dilute hydrofluoric acid to remove alteration products from the mineral surfaces. Any tourmaline in the concentrate could be removed by flotation with an amine hydrochloride in a circuit acidified with sulphuric acid. Concentrates containing 10% of Be were obtained from ores containing 0.35%, with a recovery of 70%. Tests, also by the United States Bureau of Mines,<sup>5</sup> on ten ores containing chromite or chromium spinel from the western states of America indicated the recoveries of 60 to 90% could be secured by table concentration. Modern copper concentration practice is described by Cody,<sup>6</sup> who has given an account of the treatment at the concentrator of the Morenci reduction works of 45,000 tons per day of medium-hard monazite-porphyry carrying 1.3% of chalcocite and 5.26% of pyrite, with some covellite. The ore is all ground so that 60% passes through a 200-mesh sieve and is then treated by air flotation in four series of cells—432 primary and secondary roughing cells, 72 primary cleaning cells, and 100 cleaning cells. Enormous quantities of water are needed, about 50 million gallons being in daily use and the reclamation of this is a major concern of the plant. Six tailing dams are needed, and these occupy 3.15 square miles in the Morenci and Stargo Canyons. Milling practice at Idarado (Colorado) Mining Company, where the copper occurs in a quartz gangue, has also been described.<sup>7</sup>

Flotation practices for the treatment of sulphide gold ore at Lake Shore Mines, Ontario, and of low-grade siliceous ores containing sulphotellurides at Golden Cycle Corporation, Colorado, have been outlined by Williamson<sup>8</sup> and Keil<sup>9</sup> respectively.

Flotation schemes have been worked out<sup>10</sup> to treat gravity lead-zinc ore tailings from the dump at the Grasselli mine at Park City, Utah, 30–40% of the zinc and lead being recovered as a concentrate containing 25% of lead, 5.75% of zinc, and some gold and silver values. The gravity tailings contain only 1.0% of lead and 2.65% of zinc. At the Iron King Mine, Prescott, Arizona,<sup>11</sup> 380 tons of ore containing 2.5% of lead and 7.6% of zinc are treated daily by flotation; and at the new lead-zinc concentrator of Phelps Dodge Corporation 450 tons of lead-zinc ore

containing galena, sphalerite, and pyrite are treated<sup>12</sup> each day. Here mineral separation difficulties include activation of sphalerite by copper salts, the presence of tarnished galena surfaces and interlocked minerals, and the extreme fineness of the sphalerite. The feed is ground so that 68% will pass through a 200-mesh sieve. Thiocarbonyl is the preferred collector, being more selective and yielding higher grade concentrates than sodium ethylxanthate. Three pilot concentrating tables are included in this plant so as to permit control of changing conditions in the different circuits.

The United States Bureau of Mines has continued to show interest in the possibility of developing domestic sources of manganese and has reported the results of beneficiation tests on a number of ore deposits. In Lincoln County, Nevada, low grade ores consisting of mangano-siderite and mangano-calcite intimately mixed with iron oxides and other minerals were examined,<sup>13</sup> but heavy losses of manganese occurred as a result of sliming during concentration and flotation, and the results were not encouraging. Only slightly better recoveries were obtained in tests on ores from ten mines in Grant and Emery Counties, Utah.<sup>14</sup> Here the ores consist of manganese oxides finely disseminated through a quartz gangue from which it is difficult to liberate them. Gravity concentration results in excessive losses in the tailing, whilst flotation yields concentrates with too much silica. However, from several of the ores, concentrates yielding sinters containing 35% of manganese were obtained by gravity or flotation methods and three of the ores gave concentrates from which high-grade sinters containing over 45% of manganese could be obtained with 70% recovery of manganese. Finally, in Havasu Lake district, California and Arizona, it was found<sup>15</sup> that one high-grade oxide ore containing 33.7% of manganese could be concentrated by combined sand-tabling and slime-flotation to give an 87.7% recovery of manganese in a concentrate which, after sintering, contained 48.7% of manganese. Other lower-grade ores in the same district were difficult to concentrate owing to intimate association of manganese and iron oxides, but some success was achieved by various crushing and washing or flotation treatments.

### Process metallurgy

In recent years, notable advances have been made in the study of the physical chemistry of reduction processes. A symposium on the subject, organised by the Faraday Society, provided a comprehensive survey of modern views and recorded the results of some important original work; unfortunately, the papers are not yet available in final form. One of the most interesting of the new processes is that under development at the Fulmer Research Institute for the refining of aluminium by the formation and thermal decomposition of its monohalides (a process which has been termed "catalytic sublimation"). In this connection, it is of interest to find that Kubaschewski<sup>16</sup> has described experiments carried out in Germany, presumably during the war, on the production of magnesium and aluminium by thermal reduction of their chlorides with hydrogen. He points out that the production of magnesium by the reaction  $\text{MgCl}_2 + \text{H}_2 = \text{Mg} + 2\text{HCl}$  does not appear feasible, even at

2100° K., since at this temperature energy-of-formation data indicate that the equilibrium partial pressure of magnesium vapour is still only 47.2 mm. of mercury. Calculations made for the reaction  $\text{AlCl}_3 + 1\frac{1}{2}\text{H}_2 = \text{Al} + 3\text{HCl}$  show, however, that at above 1000° K. the reaction proceeds in the gas phase, the aluminium being liberated in liquid form at temperatures above 2430° K. and in gaseous form at higher temperatures. It is concluded that conditions could be established for the continuous reduction of  $\text{AlCl}_3$ , but that the temperatures needed would be high.

One of the main sources of cobalt is still the Belgian Congo, and the electrometallurgical practice there for producing cobalt and copper has been described.<sup>17</sup> A white alloy containing 42% of cobalt is made by reducing concentrates, scoria, and dross with lime and coke in an electric arc furnace and is granulated into water. A purified electrolyte for refining is produced from hydrated cobalt oxide, precipitated by addition of lime from an impure solution, and cobalt is deposited on iron plates from which it is stripped and melted.

In copper metallurgy, great interest continues in the recent developments in Northern Rhodesia, and full accounts have been published of the Mufulira<sup>18</sup> and Roan Antelope smelters.<sup>19</sup> The Mufulira smelter is designed for an output of 10,000 tons of blister copper per month when treating a wet flotation concentrate containing about 53% total copper and 0.9% oxide copper. Two reverberatory furnaces, three Peirce-Smith converters, and two straight-line casting furnaces are provided, and copper recovery averages 97.5%. The greatest trouble which has been experienced in operation has been to reduce the bismuth content to less than 0.0025% to make the product acceptable to fire-refiners in Great Britain. Bismuth is removed during the converting operation, apparently by fuming, accelerated by the agitating operation of the air streams through the molten matte. A high temperature and a long time of blowing to the "white metal" stage are needed; the lower the grade of matte the higher is the degree of bismuth elimination. Once sufficient metallic copper is formed to act as an avid collector of bismuth, elimination ceases. Under conditions favourable for bismuth removal, the refractory linings have a short life. A successful technique has, however, been evolved. The Roan Antelope smelter commenced operations in 1931 and now contains three reverberatory furnaces, four 12 × 20 ft. Peirce-Smith converters, one holding furnace, and two straight-line casting machines. The same problem of bismuth removal is encountered as at Mufulira, and much the same procedure adopted. In order to reduce the grade of the matte (and so increase blowing time in the converters), duff coal is often added to the reverberatory charge; but as the effect, produced in this way, is limited, barren iron pyrites must often also be charged.

The very different converter practice at Rio Tinto has been described by H. R. Potts.<sup>20</sup> Here, redesigned wind boxes have been introduced and have reduced the blowing time necessary to convert all FeS into FeO from 26 to 11.5 minutes per ton. The converter copper is rarely more than 99% pure and usually contains a little  $\text{Cu}_2\text{S}$ . A laboratory study<sup>21</sup> of the reaction between cuprous oxide and synthetic copper reverberatory slags at 1200° C., reported by Huang and Hayward, shows that copper

may be lost due to formation of  $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ . Solidified slags, in this investigation, were examined by microscopical and X-ray methods.

A theoretical study of the mechanism by which gold is dissolved in cyanide solutions has been given by Thompson.<sup>22</sup> Solution of gold is shown to occur by the formation of anodic and cathodic areas when the oxygen content of the cyanide solution is non-uniform. In the extraction of gold from ores, differential aeration is best secured by brisk aeration followed by a period of rest. Addition of froth-flotation reagents is also suggested so that air bubbles may form centres of oxygen supply. Problems which have arisen in the treatment at the Sub Nigel of gold ore containing pyrrhotite, which tends to rob the solution of oxygen, have been described.<sup>23</sup> Recoveries have been improved, and the cyanide consumption decreased, by aeration in a 48 ft. deep pachuca tank. Alkalinity is maintained at the equivalent of 0.002% of CaO ( $p_H$  9.6), except in the last agitator, where it is raised to the equivalent of 0.01% of CaO to assist filtration and prevent precipitation of gold.

Improvements which have been introduced at El Paso smelter in the treatment of lead drosses have been described by Collins.<sup>24</sup> Molten lead from the blast furnace is transferred from the settler to a brick-lined drossing kettle where it is stirred with soda ash in an amount equal to 3–5% of the weight of dross. The dross is then removed and smelted in a reverberatory with sulphur, baghouse fume ( $\text{PbO}$ ), and coke to produce lead containing only about 0.2% of copper, with speiss and soda matter having a high Cu/Pb ratio. A new process<sup>25</sup> of vacuum de-zincing has been developed for removing the zinc remaining in lead after de-silvering. A bell-shaped member open at the lower end is partly immersed in the lead, which is heated to 580–590° C. The pressure in the bell is reduced to 0.5 mm. and the zinc distills and condenses on the upper parts, which are water-cooled. More than 90% of the zinc and all the cadmium are recovered from a charge of 110 tons in 5 hours.

Great interest continues to be shown in the refractory metals, titanium and zirconium. Titanium has most usually been produced by reduction of the chloride with magnesium in an atmosphere of helium or argon, and the operation of the process on a relatively large scale has been described by Kroll and Schlecten.<sup>26</sup> Zirconium has been produced by the same method, but difficulties are encountered owing to the greater sensitivity of the metal to embrittlement by oxygen or nitrogen. Kroll and his associates<sup>27, 28</sup> have given an account of a technique which they have developed for producing quantities of 60 lb. of zirconium sponge per cycle. Zirconium tetrachloride is made by chlorinating zirconium carbide and purified by sublimation in hydrogen to eliminate  $\text{ZrO}_2$  and iron. After reduction with magnesium, excess magnesium and magnesium chloride are removed by vacuum distillation. The zirconium powder is briquetted and melted in graphite crucibles in a graphite-resistor vacuum furnace.

The Van-Arkel process, in which the iodides are decomposed on a hot filament at low pressures, is particularly suited for producing both these metals in a state of high purity, although it has been used hitherto principally for zirconium. A glass unit has recently been constructed at the Battelle Memorial Institute, Ohio, for producing pure malleable

titanium, and its operation has been described.<sup>29</sup> The metal is obtained as rods 0.3–0.4 in. in diameter, weighing 300 to 600 grams each.

### Melting, casting, and fabrication

A most interesting feature of modern metallurgical practice is the evolution during recent years of a practical method of continuous (or, rather, semi-continuous) casting. The idea is old, and Sir Henry Bessemer is known to have experimented with a process in which molten metal was poured between two revolving rolls, mounted horizontally side by side, with the object of producing directly a continuous length of rolled strip. Very great difficulties are encountered in operating such a process, and attention has slowly been directed to less ambitious schemes in which the metal is poured into a short water-cooled shell mounted above a hydraulic ram which is lowered so as to withdraw the ingot from the shell as fast as it solidifies. The process has so far been applied chiefly to the casting of aluminium and aluminium alloys and two German machines have been described by Kastner.<sup>29</sup> An account of the production of duralumin billets by continuous casting, by Jean Marie Peloutier,<sup>30</sup> contains details of the moulds, water-cooling arrangements, and the clearances between mould and moving base. The speed at which the ingot can be withdrawn depends on the material to be cast. Pure metals, such as aluminium, obviously show no segregation, they do not crack, and they can be poured at high speed; some alloys, such as duralumin, are prone to segregation and need more careful handling; and others, *e.g.*, aluminium–magnesium–zinc–copper alloys, are very sensitive to cracking and are the most difficult to cast. The influence of rate of cooling on the properties of the sheet produced from aluminium alloy containing copper 3.54, magnesium 1.33, and manganese 0.64%, continuously cast by the “Wasserguss” process has been studied by Bothmann and Vosskühler.<sup>31</sup> Cracking occurred at low casting speeds, while with high speeds the long side of the ingot (500 × 165 cm. in cross-section) bowed in the middle. The defect could be overcome by redesigning the water-cooled shell. Appreciable segregation of copper was observed, particularly at high casting speeds, but the material had good rolling properties and unimpaired mechanical strength. The general advantages of continuous casting in improving quality have been summarised by Roth<sup>32</sup> as (a) reduction in oxygen and nitrogen pick-up, (b) elimination of hydrogen porosity, (c) prevention of inverse segregation, (d) absence of “coring,” and (e) elimination of piping and shrinkage voids.

Aluminium and aluminium alloys cast by the continuous process are poured from a ladle or furnace into a mould and the ingots do not usually have a section of less than about 16 sq. in. Recently, however, Smart and Smith<sup>33</sup> have described a modified process by which copper and copper alloys may be cast in sections from 0.14 to 16 sq. in. in cross-section. In this, the Asarco process, the mould or die is integrally connected to the bottom of the furnace and is fed by gravity as the solidified shape is withdrawn. It is claimed that the product has unusual soundness and malleability.

Vacuum melting and casting continue to receive some attention and more lip service. Equipment for casting ingots of copper weighing 40 lb.

*in vacua* at pressures of  $5 \times 10^{-3}$  mm. has been described by Stauffer, Fox, and Di Pietro,<sup>34</sup> who claim that the product is more ductile than other grades of copper. Experimental work on vacuum-melting and casting of beryllium in an attempt to produce sound castings has been reported by Kauffmann and Gordon.<sup>35</sup> The method finally adopted here was to distil away volatile impurities by melting in vacuum and then to cast in an atmosphere of argon. Beryllia crucibles were used for melting and a number of special constructions adopted to ensure directional solidification of the resulting ingots.

Gas porosity is an ever-present concern of the foundry metallurgist. The reactions which may cause gas to be evolved during the solidification of a metal have been comprehensively reviewed by A. J. Phillips,<sup>36</sup> particular attention being given to equilibria in the Cu-S-O, Cu-H-O, Cu-C-O, and Cu-S-H-O systems. The point is made that all well-defined gas-metal reactions can be explained on the basis of simple equilibrium chemistry since equilibrium conditions are approached closely in all molten metals. Phillips considered that there is now need for more exact determinations of the solidus boundaries in gas-metal systems.

Pinhole porosity in an aluminium alloy (RR 50) has been studied by Griffin and Stephens,<sup>37</sup> who found that while moisture in the furnace could act as a source of hydrogen, sound castings could be obtained even under adverse conditions by using a NaCl-NaF flux. An unusual method of degassing aluminium alloys has been described by Esmarch, Rommel, and Benthner,<sup>38</sup> who claim that if the alloy is melted in an induction furnace all gas is removed in 30-60 minutes by superimposing a magnetic field on the high frequency field of the furnace, provided that the melt is covered by a molten flux and that dry air or nitrogen is directed on the surface. In this connection, it is important that the solubility of hydrogen in liquid or solid aluminium should be accurately known. Attention may thus be directed to the careful redeterminations of these values by Ransley and Neufeld,<sup>39</sup> who find that the solubility  $S$  (c.c. per 100 g. of metal) in the liquid is given by  $\log_{10} S/P^{\frac{1}{2}} = -2760/T + 1.356$ , where  $P$  is the hydrogen pressure in mm. of mercury and  $T$  is the absolute temperature. This applies between  $670^{\circ}$  and  $850^{\circ}$  C. In the solid, between  $465$  and  $620^{\circ}$  C.,  $\log_{10} S/P^{\frac{1}{2}} = -2080/T - 0.652$ .

The extensive literature on unsoundness in copper-base alloys has been critically reviewed by Eastwood and Kura<sup>40</sup>; and in this country Pell-Walpole<sup>41</sup> has given an up-to-date account of his work on the use of oxidising fluxes for degassing bronzes. In a recent investigation he reports that high-phosphorus, zinc, and lead bronzes were effectively degassed by melting under mixtures of cupric oxide, fused borax, and sand. Discussing these results, Baker<sup>42</sup> has pointed out that in the investigations of the British Non-Ferrous Metals Research Association it was found that oxidation of hydrogen by fluxes was retarded if phosphorus or more than 0.5% of zinc were present in the metal. There is, however, a difference between the two sets of investigations. The Pell-Walpole process has been applied to chill castings and he has agreed that his conclusions do not necessarily relate to sand castings, as used by Baker, since these may absorb hydrogen from the mould.

A most interesting investigation into the cause of gas-unsoundness in

nickel-silver castings has been reported by Pearson, Baker, and Child.<sup>43</sup> These alloys contain about 20% of zinc, and it is difficult to understand how hydrogen, the common prime cause of gas unsoundness in copper-base alloys, can remain in solution in view of the very high vapour pressure of zinc at the temperatures at which the alloys are molten. It is, in fact, found that the gas unsoundness in nickel-silver alloys (containing copper 60, zinc 20, nickel 20%) is caused by the evolution of carbon monoxide during solidification. Carbon and oxygen can apparently co-exist in solution in the molten alloy, but combine during solidification. The gas-unsoundness may best be eliminated by melting under strongly oxidising conditions to remove carbon. De-oxidation is recommended as an additional precaution, but very powerful de-oxidisers appear necessary to reduce the oxygen content below the critical value.

Although so much effort needs to be exerted to eliminate gases from cast metals, it has nevertheless to be recognised that in some circumstances small amounts of well-distributed gas may be desirable and may tend to prevent the formation of dangerous-shaped contraction cavities. The effect of dissolved gas on the hot-tearing of aluminium casting alloys has been investigated by Lees,<sup>44</sup> who found that a ternary alloy with silicon 5 and copper 3% (DTD 424) was rendered immune from hot-tearing by a moderate gas content. In other alloys, however, a gassing treatment was less effective, and a binary alloy with 4% of copper was just as prone to the defect when the melt was saturated with hydrogen before pouring as when it was gas-free. Generally speaking, hot-tearing appears to be affected more by the eutectic content than by gas treatment.

### Metallography

"The art of metallography is mature and the forms in which various micro-constituents appear are well known. . . . Surprisingly, however, comparatively little attention has been paid to the forces that are responsible for the particular and varied spacial arrangement of grains and phases, observed." These words were used by Professor Cyril Stanley Smith,<sup>45</sup> Director of the Institute for the Study of Metals at the University of Chicago to introduce the 1948 American Institute of Metals Division Lecture in which he developed in considerable detail the view that surface tension forces may be an important determining factor, hitherto largely disregarded, in many metallurgical processes. Particular attention is paid to the shape of the dihedral angle formed in two-phase alloys at the junction of a crystal of one phase with two crystals of a second phase in a well annealed alloy, and it is shown that this is very nearly constant for each system. The results of measurements on a number of three-phase systems are also tabulated. Surface tension forces may also play an important rôle in solidification processes by ensuring that all surfaces of a growing crystal are continually wet. Thus, even though two growing crystals meet each other and consume all the liquid originally between them, growth will continue by capillary feeding to the interface, which will eventually become a grain boundary. This view explains why crystals in the interior portion of ingots have the shape demanded by surface tension and not that which would be expected to result from uniform growth from randomly-occurring nuclei. The

new viewpoint opened up by this paper seems likely to have an important influence on metallographical theory.

Several investigations have been reported concerning transformations in pure metals. Troiano and Tokich<sup>46</sup> have studied the change from the hexagonal to face-centred cubic form in the structure of cobalt which occurs at about 500° c. Cobalt can be brought into the hexagonal form at room temperature by moderate deformation, and becomes cubic at above *ca.* 500° c. Hitherto, there has been some doubt as to whether cobalt can be retained completely in the cubic form at room temperatures by quenching. Working with filings from cobalt sheet, these investigators find that deformed filings will remain cubic after quenching from 425–700° c. but only if they are maintained at the high temperature for a sufficiently long time. The effect is ascribed to grain growth, and it is further suggested that the hexagonal form is not stable but is a transitional structure formed by a martensite type of transformation. The transformations in cerium and the effect of these on the impurities present in the commercial metal have been studied by Trombe and Foex.<sup>47</sup> Considerable differences were found between the two materials, and these are ascribed chiefly to the influence of calcium; iron and silicon do not appear to go into solid solution with cerium. A low-temperature transformation has been reported in lithium by C. S. Barrett.<sup>48</sup> This occurs on plastic deformation at –196° c. and results in the formation of a face-centred cubic modification with a lattice spacing of 4.41 Å. The transformation is accompanied by a series of audible clicks, as in the twinning of tin and magnesium, from which it is concluded that the process takes place by abrupt shear movement in small isolated regions. A partial transformation at about the same temperature in unworked lithium and lithium-magnesium alloys has also been observed.<sup>49</sup> In lithium, the low-temperature structure is tentatively identified as close-packed hexagonal. In the lithium-magnesium alloys it apparently differs from this, although the diffraction pattern is very similar to that of close-packed hexagonal lithium.

A great deal of attention has been given to problems concerned with recrystallisation and grain growth in metals and alloys. In particular, the causes of "secondary recrystallisation" or discontinuous grain growth have been a fruitful subject of discussion. This is the phenomenon, occasionally observed, by which a few very large grains develop in a relatively fine-grained matrix on prolonged annealing. Very often the large grains make their appearance only after long periods of incubation. The influence of preferred orientation on the phenomenon has been studied by Bowles and Boas,<sup>50</sup> who found, in experiments on copper, silver, and two grades of aluminium, that isolated large grains could be grown regardless of the mode of arrangement of the original crystals, but that it occurred more rapidly, the greater the similarity between their orientations. They concluded that preferred orientation makes it more easy for selected large crystals to grow but does not appreciably influence their rate of growth. These workers tacitly accepted the view, originally advanced by W. G. Burgers, that secondary recrystallisation is the result of the growth of "nuclear spots" which persist unchanged throughout the initial stages of recrystallisation and only become active after a

prolonged period of annealing. The paper produced a vigorous discussion when it was presented at the Institute of Metals meeting at Cambridge, and many speakers took the view that discontinuous grain growth may be caused by the occasional breakdown of barriers to grain-growth, the barriers being considered to be inclusions or other dispersed phases. Further support for this view has since appeared in the form of a detailed study<sup>51</sup> of the influence of finely-dispersed aluminium-manganese compound on grain growth in aluminium-manganese alloys containing 0.25-1.6% Mn. In these alloys, it was observed that when particles of the compound were present the grain boundaries were often strongly curved and tended to adhere to the particles. Moreover, discontinuous grain-growth or coarsening could be produced at will by annealing at such a temperature that some of the particles were slowly re-dissolved and others coalesced. The large grains did not form at once under this treatment, but only after an incubation period of from one to 55 days. Thus it seems that the condition essential for discontinuous grain-growth is the gradual removal or absorption of blocking agents which have been present initially in the alloy.

The more straightforward phenomena of recrystallisation and grain-growth in cold-worked metals still offer scope for investigation. Laurent and Batisse<sup>52</sup> have determined curves of isothermal recrystallisation at 343-393° C. by measuring the hardness of specimens heated to the same temperature for various times. Isothermal grain-growth in 70-30 brass has been investigated by Beck, Towers, and Manly<sup>53</sup> for annealing periods extending to 11 days at 450, 500, 600, and 700° C. The results for this alloy can be represented by  $D = K.t^n$  where  $K$  is constant for a given temperature and  $n$  is  $0.212 \pm 0.010$  for the whole temperature range from 450° to 700° C. Similar determinations<sup>54</sup> have been made on pure aluminium at 350-600° C. Demer and Beck<sup>55</sup> have also commenced a systematic study of the effect of composition on grain growth in aluminium-magnesium solid solutions. Here, the results are best expressed as  $D = D_r/R^n.t^n$  where  $D_r$  is the grain-size as recrystallised after time  $R$  and  $n$  depends on the temperature and the material,  $D$ , is, of course, the grain-size after a total annealing period,  $t$ . Tests on alloys containing 0.025, 0.12, and 1.8-2.05% Mg indicate that  $n$  changes little up to 0.025% Mg and then increases linearly with the logarithm of the magnesium content. The recrystallised grain size, at 350° and 400° C., is also unaffected by magnesium content up to 0.025% and then decreases linearly with the logarithm of the magnesium content.

The nature of crystal boundaries has remained a subject for experiment and speculation. A series of papers by T'ing-Sui Kê,<sup>56</sup> putting forward the view that the transition region between adjoining grains can behave in a viscous manner, has attracted considerable attention. The evidence, which has been derived mainly from relatively simple tests on the damping of wire specimens in torsional oscillation, indicates that the activation energy associated with grain-boundary slip is close to that for diffusion or self-diffusion. Grain-boundary slip is regarded as creep on a microscopic scale and it is suggested that it occurs at a lower temperature than trans-crystalline creep because of the disturbed structure at the crystal boundaries. In this country, the results of pressure and creep

tests at constant hoop stress on lead and lead alloy pipes have been discussed by Latin<sup>57</sup> and are interpreted as providing evidence for boundary flow. Further experimental work has also been reported by Chaudron, Lacombe, and Yannaquis<sup>58</sup> on the old question as to whether the melting point of the grain boundaries of a pure metal is lower than that of the body of the crystals. Aluminium of 99.99–99.998% purity was used, and a temperature-gradient applied to an electrolytically-polished specimen. The areas affected by fusion were subsequently revealed by attack with 30% hydrochloric acid. The results are considered to support the view that melting commences at the crystal boundaries. It is reported, however, that after heating near the melting point for 15 hours, an unexpected change occurs and the acid then attacks the crystals and leaves the grain boundaries unaltered, giving a honeycomb structure.

Interest in single crystals as such has not been very marked during the year, but it may be noted that a simple method of growing single crystals of aluminium has been described by Lacombe and Beaujard.<sup>59</sup> An aluminium sheet is simply heated on a clay slab in a muffle furnace in which a temperature gradient of about 10° c. is maintained from end to end. The sheet melts but is held to its shape by the oxide skin. The temperature is then lowered slowly and the aluminium, after supercooling, solidifies suddenly from the cooler edge and forms, in about one experiment in three, a single crystal.

## Non-ferrous metals

### *Constitution*

An unusually large number of investigations, many of them conducted with considerable skill and care, on the constitution of alloy systems have been described. The aluminium–zinc–manganese system in the range up to 95% of zinc and up to 3% of manganese has been studied by Raynor and Wakeman,<sup>60</sup> who have identified the many complex phases by first extracting them by electrolytic attack and then examining them by microscope, X-ray, and chemical methods. The phases which occur as the composition is changed along the eutectic valley from the aluminium corner towards the ternary eutectic are, successively,  $\text{MnAl}_6$ ,  $\text{T}_1$ ,  $\text{MnAl}_4$ ,  $\text{T}_2$ ,  $\text{T}_3$ , and  $\text{MnAl}_3$ . The compound  $\text{T}_1$  is analogous to the ternary compounds observed in the aluminium–manganese–nickel and aluminium–manganese–copper systems,  $\text{T}_2$  can be represented as  $\text{Mg}_2\text{ZnAl}_9$ , and  $\text{T}_3$  as  $(\text{Mn.Zn})_5\text{Al}_{11}$ . Special theoretical interest attaches to the compounds of the type  $\text{T}_1$ , which are all based on a ratio of aluminium to solute atoms of 4 : 1 and have an electron/atom ratio of 1.85, since it seems probable that the vacancies in the atomic orbitals of the transitional metal are filled by electrons absorbed from the structure as a whole. Compounds of this type can, however, only be expected if the atomic-size relationships are suitable. An examination of the aluminium–manganese–cadmium system<sup>61</sup> showed that no ternary compound was formed in equilibrium with the aluminium-rich solid solutions. The cadmium atom is so much larger than the zinc atoms that the size relationship cannot be satisfied. Further studies<sup>62</sup> have also been made on the aluminium–manganese–magnesium and aluminium–manganese–silver systems. No ternary compound of the type  $\text{T}_1$  is found when silver is

substituted for zinc; and, when magnesium is substituted, a ternary compound of a different type, with an electron/atom ratio of 2.37 instead of 1.85, is formed.

At Oxford, Hume-Rothery<sup>63</sup> and his colleagues have continued their work on aluminium-base alloys of various degrees of complexity. Interest has previously been shown in a metastable phase, denoted G, which these investigators have found in pure aluminium-manganese alloys containing a few per cent. of manganese when the alloys are annealed at not too high a temperature. They now find that the addition of silicon and iron in small amounts (about 0.2%) completely suppresses the formation of the G phase, and that chromium is the only one of a number of elements examined which causes G to become a stable constituent. It appears improbable that the G phase will be found in alloys of commercial purity. The very complex equilibria in the quaternary system aluminium-copper-magnesium-zinc have been investigated,<sup>64</sup> a temperature of 460° c. being chosen for a first survey, and the phases which are present in samples annealed for long periods identified by microscopic examination. In the alloys studied, only phases which are the same as, or are derived from, those of the three ternary systems have been found and no new quaternary phase has been encountered. The diagrams which present the results of this work represent one of the most complete attempts yet made to delineate the phase boundaries in a quaternary system. The Oxford investigators have even gone so far as to tackle quinary systems and have examined<sup>65</sup> the effect of 1% of silicon on the constitution of aluminium-magnesium-manganese-zinc alloys at 460° c. The effect of this amount of silicon on the melting points of alloys in the same system<sup>66</sup> has also been studied, and it is found that if there is less than 1 or 2% of magnesium the melting point may be lowered by as much as 75° c.; but that if the magnesium content is above 4%, the addition of 1% of silicon does not decrease the melting point and may increase it appreciably. The effects of chromium additions to the alloys have aroused some interest and as a preliminary to a fuller investigation, the constitution of the aluminium-magnesium-zinc-chromium system at 460° c. has been determined<sup>67</sup> for magnesium contents of up to 20% and zinc and chromium contents of up to 10%. Great difficulties were found in attaining true equilibrium, even after very prolonged annealing treatments. In the cast state, many of the alloys contain crystals of the  $\text{Cr}_2\text{Al}_{11}$  phase surrounded by sheaths of the stable phase,  $\text{CrAl}_7$ , and annealing periods of the order of two months are required for the removal of the  $\text{Cr}_2\text{Al}_{11}$ .

In France, two commercial alloys, one in the aluminium-zinc-magnesium and the other in the aluminium-zinc-magnesium-copper system have been examined after various heat treatments by Saulnier,<sup>68</sup> and the mechanism of their age-hardening discussed.

The aluminium-rich region of an unusual system, that of aluminium and sodium, has been investigated<sup>69a</sup> by Fink and his associates in America. The liquidus falls smoothly from the melting point of aluminium, 660.2° c., to a monotectic at 659.0° c. and 0.18% sodium. The solubility of sodium in solid aluminium was found to be less than 0.003% at 659° c., and probably decreases at lower temperatures.

A copper alloy system of some industrial importance is that of copper-chromium, since alloys containing 1% of chromium or less can be heat-treated to throw nearly all the chromium out of solid solution and so develop a combination of high mechanical strength and high electrical conductivity. A re-determination of the solid solubility curve, by Hibbard,<sup>69</sup> has confirmed Alexander's results, published in 1939, and the eutectic is now placed at 1069–1072° C. with somewhat more than 1.33% of chromium. The effects of additions of up to 30% of nickel have also been investigated. The copper-rich corner of the copper-aluminium-silicon system has been studied by Wilson,<sup>70</sup> who finds that the *K* phase of the copper-silicon system persists in the presence of as much as 8.5% of aluminium.

The cobalt-chromium system is the basis of a group of high-temperature alloys widely used in the construction of gas turbines, but there have hitherto been important unreconciled differences between the diagrams put forward by various workers. A careful re-determination of the binary diagram was undertaken at the Battelle Memorial Institute, Columbus, Ohio, under the sponsorship of the Office of Naval Research, U.S. Navy, and the results have now been published.<sup>71</sup> Experimentally, the most troublesome part of the work was the avoidance of pick-up of nitrogen, and it was necessary to carry out all melting and heat-treatment operations in purified argon from which nitrogen was removed by passing the dried gas through a container packed with titanium metal granules heated to 750° C. The revised diagram is presented as a result principally of metallographic studies of specimens heat-treated at different temperature, X-ray diffraction analyses being used to identify the phases and make it possible to develop suitable etchants.

A study of the gold-platinum system, reported by Carl-Gustav Wic-torin,<sup>72</sup> is of more theoretical interest. The limits of the two-phase region below the solidus were carefully re-determined by electrical resistance measurements, and the results are applied thermodynamically to test the theory of Borelius that precipitation must be preceded by a local concentration, caused by thermal fluctuations, of one of the components of the alloy system.

Among other systems studied were those of aluminium indium,<sup>73</sup> cerium-nickel, lanthanum-nickel, praeosodymium-nickel, and cerium-cobalt,<sup>74</sup> cerium-magnesium, and lanthanum-magnesium,<sup>75</sup> and the ternary system gold-nickel-copper.<sup>76</sup> The latter system is of particular interest in view of the order-disorder changes which occur.

Finally, reference should be made to the excellent comprehensive collection of binary and ternary diagrams in the 1948 edition of the *Metals Handbook*.<sup>77</sup> These diagrams comprise the first such collection to appear in a publication in the English language since 1927, they have been carefully and critically compiled, they are up-to-date, and likely to be widely consulted by metallurgists.

### Metals under stress

The metallurgical study of metals under stress borders on engineering on the one hand and on theoretical physics on the other. The engineering

approach is seen in such papers as that by Dudzinski<sup>78</sup> and his colleagues at the Royal Aircraft Establishment, Farnborough, describing a search for aluminium alloys having a high value of Young's modulus. These workers conclude that the modulus of aluminium may possibly be increased from about 10 to above  $12 \times 10^6$  lb./sq. in. by suitable additions of manganese, nickel, and, perhaps, other elements in small amounts. Of engineering interest also is an examination by Voce<sup>79</sup> of the relationship between stress and strain for "homogeneous deformation," *i.e.*, for deformation in which all parts of the specimen are deformed to the same extent and in the same manner. This mode of deformation is that produced by compression if friction between the ends of the specimen and the compression blocks is eliminated, and it is shown that the plastic modulus (the rate of change of stress with respect to true, logarithmic, strain) at any instant is proportional to the available stress capacity. Some important papers have been published on damping-capacity, of which the precise engineering significance is still a matter of controversy. A review of damping-capacity determinations on ferromagnetic and other metals by a number of methods has been given by Potter,<sup>80</sup> and in this country, Cottell, Entwistle, and Thompson<sup>81</sup> have described a careful experimental study of testing methods carried out under the auspices of the British Non-Ferrous Metals Research Association. The results show conclusively that the measured damping values which have been observed in the past with machines of the Föppl-Pertz type may be of the order of 500 or more times the true damping-capacity of the material, since the machine losses completely mask the contribution made by the test specimen itself. This is considered to account for the discrepancy hitherto found between the results of "mechanical" and "physical" methods of measuring damping-capacity in torsional vibration. A new design of machine has been developed and, with this, measurements of the damping-capacity of duralumin have been found to be in excellent agreement with the lowest values found by physical methods. Fatigue tests have received less attention recently than in recent years, but studies have been reported of the fatigue properties of some magnesium sheet alloys,<sup>82</sup> beryllium-copper strip,<sup>83</sup> and of the notch-sensitivity in fatigue loading of some magnesium-base and aluminium-base alloys.<sup>84</sup>

Of more physical interest are the important developments which have been made in the theories of plastic flow in metals, and in particular in the theory of dislocations. In the past, it has been considered that, during deformation, adjacent blocks of each metal crystal glide bodily past one another along the slip planes. However, great discrepancies are found between the shear stresses calculated to effect such a movement and those actually observed; and much more satisfactory agreement has been secured by postulating that small imperfections or dislocations exist in all metals and that under stress these are caused to move through the crystal along the slip direction with the speed of sound, each dislocation being attended by a local shear displacement of one atomic distance. Thus it is now considered that a slip-band does not suddenly appear in its entirety but grows progressively across the slip-plane as the individual dislocations successively appear and advance in a train through the crystal.

Some aspects of the theory, and in particular its application to the study of transient creep in age-hardened alloys have been discussed by Mott and Nabarro<sup>85</sup> in a paper summarising the content of lectures given at a summer school at the University of Bristol. In a note read at the same conference, Sir Lawrence Bragg<sup>86</sup> develops the view that slip must take place by at least a complete jump equal to one interatomic distance and that slip in each crystal element must be regarded as an individual process, the surrounding matrix remaining fixed while it takes place. Some interesting complications may arise in solid solutions in which the solute atoms are different from the solvent atoms in size and these have been examined by A. H. Cottrell.<sup>87</sup> The individual solute atoms are obviously centres of strain, but as they can migrate as a consequence of thermal agitation, the internal stresses, which they provide, relax as the atoms migrate. They will accordingly cluster round dislocations forming "atmospheres" similar to the ionic atmospheres of the Debye-Hückel theory of electrolytes. It may thus be supposed, as K. W. Andrews has pointed out in discussion, that in every solid solution there is a state approaching semi-precipitation round every grain boundary and the boundaries of mosaic all blocks (viewed as regions of high dislocation density); and it is possible to explain on this viewpoint such phenomena as strain ageing and yielding in iron containing small amounts of carbon or nitrogen. Further support to the theory of dislocations is given by R. L. Woolley,<sup>88</sup> who describes the behaviour of reversed torsion tests on thin-walled copper tubes. The shape of the stress strain curve is considerably modified by previously applying strain in the reverse direction; and this behaviour can most easily be explained on the grounds of exhaustion of the dislocations. A theory of deformation which is somewhat allied to the dislocation theory considers that a metal may be deformed by the migration of vacant lattice sites. A critical re-examination of this theory has now been made by Nabarro,<sup>89</sup> and he concludes that previous estimates of the rate of movement by this mechanism must be rejected since a homogeneous stress can exert no force on a vacant lattice site. A crucial test of the truth of the theory would be, Nabarro points out, to observe the creep behaviour of a metal while it was subjected to intense neutron bombardment. The bombardment would provide numerous vacant lattice sites by knocking ions from their normal places in the lattice into interstitial positions.

Some extremely beautiful experimental work on the mechanism of slip has been reported by Heidenreich and Shockley<sup>90</sup> from the Bell Telephone Laboratories, Murray Hill, New Jersey, using both electron-microscope and electron-diffraction methods. Aluminium was the metal chosen for this work, mainly on account of the ease with which anodic oxide replicas could be prepared. Tensile specimens cut from sheet were, moreover, very simply converted into single crystals by melting them in an alundum boat in air over a gas flame. The oxide film was sufficiently strong to maintain the shape while the metal was molten. The flame was then moved to one end and solidification allowed to proceed from the opposite end until the specimen was solid again. Observations were made of the slip lines formed on the electro-polished surfaces of the single crystal specimens after deformation in tension or in compression.

The electron-microscope photographs show clearly and conclusively that a slip-line, seen under an optical microscope, really consists of a number of laminae which are each about 200 Å. thick and can undergo a maximum relative displacement of about 2000 Å. The electron-diffraction patterns indicate further that the regions between the slip planes rotate slightly, one with respect to another. The importance of these observations is the clue they give to the solution of the problem as to why a metal is hardened by cold work—why glide once started on a glide surface ever stops. The implications have been worked out by F. C. Frank,<sup>91</sup> and he shows that if, indeed, the lamellae observed by Heideneich and Shockley are separated by single glide-planes, the proper description of such rotation in terms of dislocations is as an accumulation of screw dislocations in the plane. A single dislocation will thus tend ultimately to interlace a particular plane, and glide will cease when the plane has become interlaced with dislocation lines to an excessive density.

The evidence for the existence of dislocations in crystals is strengthened by the results of experiments by Haynes and Shockley<sup>92</sup> in which crystals of silver chloride were exposed to short pulses of light and a synchronised pulsing electric-field. Specks of colloidal silver were formed at points where electrons were trapped; and it was found that electron-traps occurred both at the crystal boundaries and along slip-planes. Techniques are being developed to expose these slip-planes so that electron-microscope replicas can be made. When this is done, it may be possible to see the distribution of imperfections in the slip-bands on a previously unattainable scale and thus, perhaps, to photograph actual dislocations.

Some fruitful consequences of developing the dislocation theory have also been reported from America. Since slip-bands are considered to grow, it follows that they must first be nucleated, and, accordingly, Leschen, Carreker, and Hollomon<sup>93</sup> have analysed the initiation of slip in terms of the general concepts of nucleation. In this way, they have been able to account for the periods of incubation, during which no elongation takes place, which have been observed in the early stages of deformation of crystals of iron and alpha brass at low stresses. Furthermore, they predicted that if the applied stress on a metal should be suddenly changed from one constant value to another, a transient should occur in the form of a discontinuous change in the strain-rate followed by a gradual approach to a steady-state value. Such transients have, in fact, subsequently been observed by Carreker, Lescher, and Lubahn<sup>94</sup> in lead, copper, and aluminium alloys. In a typical experiment, a lead specimen was loaded with 456 lb./sq. in. and allowed to reach a steady rate of creep of  $1.25 \times 10^{-6}$  in./in./min. On suddenly increasing the load to 468 lb./sq. in. there was a sudden very large increase in the rate of strain and this then fell slowly to a new steady value of  $3.5 \times 10^{-6}$  in./in./min. which was reached after about 30 min. When the load was suddenly reduced again to its original value, creep ceased completely for over 10 min. and the original creep rate did not develop until after about 40 min. Similar observations were recorded with the other metals. An important practical conclusion from these tests is that cyclic loads or temperatures in creep-tests produce appreciably greater strains than

do constant conditions, unless the duration of the transient effects is much less than the length of the cycle.

### Corrosion

Only a very brief survey of recent work on corrosion will be attempted. An extensive investigation, carried out in the Research Laboratories of Vereinigte Leichtmetall-Werke, Hanover, on the intercrystalline corrosion of aluminium-magnesium alloys containing 5 to 9% of magnesium was presented at the Annual General Meeting of the Institute of Metals,<sup>95</sup> and gave rise to considerable discussion. A new "stabilising treatment," in which the alloy is very slowly cooled, at about 50° C. per hour, from the homogenising temperature has been developed, and it is claimed that this confers immunity to intercrystalline corrosion and stress-corrosion failure. Criticism was directed against the testing conditions employed; the solution of 3% NaCl and 1% HCl which was principally used is extremely corrosive, and the failures when it is used for accelerated corrosion testing are undoubtedly due, at least partly, to general corrosion of the specimen. In this country they would not normally be regarded as stress-corrosion failures, and the discussion was valuable in bringing out clearly the difference between the points of view regarding stress-corrosion of aluminium alloys adopted in Germany and in this country. Exposure tests of aluminium alloys to the hot marine climate on the N. Mediterranean coast at Salin de Giraud, recorded by Beliaeff,<sup>96</sup> provide further data on the influence of heat-treatment of such alloys as duralumin on corrosion rates, and also indicate that in semi-tropical conditions the effect of sea organisms may be the most important factor influencing corrosive attack.

An extensive investigation has been commenced in this country into the suitability of various paint primers for protecting aluminium and magnesium alloys against corrosion in industrial, marine, and rural atmospheres. Preliminary results<sup>97</sup> show conclusively that red lead primers are unsuitable for light metals and may even accelerate corrosion. Zinc chromate and iron oxide primers, however, provide useful protection but further work will be needed to establish which is the better.

In condenser-tube research, there have for many years been reasons to believe that the rate of corrosion may often be influenced by bacteria, moulds, and other living organism. The results of investigations, carried out by the British Non-Ferrous Metals Research Association, into the promotion and acceleration of corrosion by micro-organisms have now been described by Rogers,<sup>98</sup> and it is shown that corrosion may take place either by direct attack, during the life of a bacterial colony closely associated with a metal surface, or by indirect attack due to the corrosive action of some products of bacterial metabolism.

The exact effect of impurities on the rate of corrosion of magnesium-base alloys is still a matter of some controversy. The quantitative implications of Hanawalt's theory to account for the effect of traces of iron and other impurities on the corrosion of these alloys in solutions of sodium chloride have been examined by Bushrod,<sup>99</sup> and although some apparent correlation was found between theory and experiment,

*a priori* reasons are given for supposing the basis theory to be incorrect. The corrosion of magnesium-base alloys of the type containing 5% of aluminium when immersed in 3% NaCl solution, both separately and in contact with other metals, has been studied by Fox and Davies,<sup>100</sup> who suggest that the galvanic corrosion of these alloys, unlike that of most other magnesium-base alloys, is controlled by cathodic reactions due to the formation of an unstable and non-adherent surface anodic film. Fox has also found<sup>101</sup> that additions of not more than 0.4% of zinc to commercial alloys of this type improves their corrosion resistance when immersed in salt water, but may increase the corrosion rate of alloys of very high purity.

A survey of the problem of the stress-corrosion (or season-cracking) of brass has been given by Chaston,<sup>102</sup> who has put forward the theory that grain-boundary attack may be localised owing to the formation of a protective film of corrosion product over the faces of the crystals. It is thought that the films may have a regular structure, protective in character, based on the underlying crystal-lattice of the alloy; but that at the grain-boundaries the structure of the film is less regular and less protective. Observations of the behaviour of stressed 9-carat gold alloys in ferric chloride solution are said to support this view.<sup>103</sup> The normal rapid cracking may be delayed by continuously brushing the surface of the specimen. The stress-corrosion of solid-solution precious metal alloys has been studied by Graf,<sup>104</sup> who considers that all solid-solutions having the less noble metal as a basis are liable to this type of attack. Only alloys in which a noble metal predominates are immune.

Basically, the simplest form of corrosion is that which occurs when a pure metal is exposed to dry oxygen; and a full understanding of the reactions which occur is of fundamental importance in such work as the development of heat-resisting alloys. Gulbransen and his colleagues at the Westinghouse Research Laboratories, have recently developed a reflection electron-diffraction technique which enables the changes in the composition of the outer layer of the oxide film to be followed when a metal or alloy is heated at a low pressure of oxygen for various times. The results of examinations of films on heat-resisting alloys containing nickel, chromium, cobalt, and iron,<sup>105</sup> titanium, zirconium, and their alloys,<sup>106</sup> molybdenum,<sup>107</sup> and tungsten,<sup>108</sup> have been published and are likely to be of considerable theoretical and practical significance.

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# ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES

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THE most notable trend in work on electrolytic processes during the past year has been the increasing application of scientific methods to the study of the properties of electro-deposited metals, especially nickel and chromium. The possibilities of alloy deposition have been receiving much attention and a notable development is the successful use of speculum plating on a commercial scale; demands for metals to resist high temperatures have encouraged work on the deposition of alloys with refractory metals such as tungsten and molybdenum. Amongst other practical developments of metal deposition, a noteworthy feature is the increasing use of electro-forming as a method of making certain types of article which are difficult or costly to produce by conventional methods with the desired mechanical properties and fine dimensional tolerances; dies and moulds for plastics or die casting, fountain pen caps and various precision parts of optical systems are examples. Electrolytic methods of producing or refining metals continue to be developed or improved; processes have been applied on a pilot scale for the production of chromium, cobalt, and manganese (from chloride solutions), while the commercial production of manganese from sulphate solutions has been described.

## Electrolytic processes

### *Extraction, refining, plating, and polishing of metals*

**Aluminium.**—During the anodic oxidation of aluminium, the oxide layer is supposed to dissolve continuously in the electrolyte at a rate which, once steady conditions have been reached, is comparable with its rate of formation. Quantitative information on the rates of formation and dissolution of the oxide layer has been derived from studies of the anodic reactions of aluminium in sulphuric and oxalic acids.<sup>1</sup> In a similar investigation,<sup>2</sup> the rate of change in weight and thickness of the metal was examined for various aluminium alloys and the formation of cracks in the film on curved surfaces was studied. The tendency of the coating to crack is increased by the presence of foreign constituents in the oxide layer but is otherwise not much affected by the composition of the metal or the conditions of anodising; it is mainly a function of the sharpness of curvature and the thickness of the oxide layer.<sup>3</sup> This tendency to crack on curved surfaces limits the insulating properties of the film which rise to a maximum not increased by further time of treatment; anodising conditions can, however, be chosen to give a flexible coating and the process can be adapted for the continuous anodising of conductors which will withstand 220 volts at 500°.<sup>4</sup> The extent to which anodically oxidised films afford protection against corrosion and their ability to accept dyes, lubricants, etc., depend on their permeability; this property

has been examined, using detached films and foil completely anodised into oxide, by measurements of salt diffusion, osmosis, conductance (with salt solutions as electrodes) and water transport. Continued exposure to the anodising electrolyte increased the permeability considerably but sealing it in boiling water decreased it a hundredfold; results of conductance tests suggested that the film is not entirely penetrated by pores but that there is a residual, relatively impervious barrier within the film.<sup>5</sup> Thick oxide films are needed for protection against wear and the film should be impregnated with a suitable lubricant; for use in internal combustion engines, films 50–500  $\mu$  have been stated to be necessary.<sup>6</sup> The thickness of anodised films on aluminium may be measured by means of a non-destructive electrical test depending on the change in inductance of a test coil with distance of separation from the aluminium surface; tests of an American instrument known as the Filmeter indicated that its accuracy was comparable with that of the usual methods of microscopic measurement or loss in weight on stripping in a hot solution of phosphoric and chromic acids<sup>7</sup>; a solution used by Siemens Halske A.-G. for stripping oxide films from aluminium is reported to contain sulphuric acid (382 g./l.) and antimony trioxide (2 g./l.).<sup>8</sup> Instructions for the anodising, dyeing and electrolytic brightening of aluminium and its alloys together with a general account of the properties of the films and a bibliography and list of patents have been issued.<sup>9</sup>

Few publications on the electro-plating of metals on aluminium have appeared during the past year but a useful annotated bibliography of this subject covering the period 1918–47 (82 references) has been issued.<sup>10</sup> Applications of electro-plated aluminium alloys include internal combustion engine cylinders with a "porous" chromium lining and silver plated parts for electrical use.<sup>11</sup> The electro-plating of aluminium on other metals has not yet emerged from the laboratory stage; three patent specifications claim electrolytes based on fused mixtures (e.g., at 125°) of aluminium chloride and ethyl pyridinium bromide or chloride.<sup>12</sup>

Additional details of the aluminium production and refining industries in enemy countries during the war have not revealed any important new information<sup>13,14,15</sup>; the three-layer process for aluminium refining, referred to in last year's Report, has been further described.<sup>16</sup> Problems involved in the electrolytic production of aluminium (heat loss, anode effect, removal of aluminium from the cell) and the construction and operation of the newest type of Soderberg electrode have been discussed in detail.<sup>17</sup> The Soderberg electrode system was introduced 25 years ago and a review of its development during this period has shown that the power efficiency has improved from 27 per cent. in the early days to 39 per cent. to-day and that there is a potential further improvement to 55 per cent. in the future.<sup>18</sup> The presence of potassium in the fused cryolite electrolyte used for the reduction of aluminium considerably lowers its surface tension with consequent disintegration of the floor of the cell; for safe operation, the alumina used should not contain more than 0.16 per cent. of  $K_2O$ .<sup>19</sup> The plant of the South Wales Aluminium Company at Resolven uses a steady load of 32,000 amps.<sup>20</sup>

**Chromium.**—One of the difficult problems of practical chromium plating has been the evolution of a satisfactory method of barrel plating. A

review of developments, illustrated with photographs and diagrams, includes a description of a horizontal type of bath barrel and of an automatic barrel which have been operated in America for a number of years using a chromic acid solution containing silico-fluoride and practically no sulphate.<sup>21</sup> Objections to this type of solution for ordinary tank operation on the grounds of short life have been disputed as a result of a large scale test in which no deterioration in current efficiency or quality of deposit was found after extensive use of the solution.<sup>22</sup> Shortage of chromic acid, both here and in America, has encouraged publications on methods of conservation.<sup>23</sup> A test to determine the sources of loss of chromic acid during plating showed that 7% was accounted for by electro-deposition as metal, 48% was lost as drag-out, and 45% was lost as spray.<sup>24</sup> Much, but not all, of the loss by spray can be avoided by the use of plastic beads floating on top of the solution<sup>25</sup> or by the addition to the solution of surface active substances,<sup>26</sup> but the use of these devices does not reduce the chromic acid in the air above the vat to less than the maximum allowable concentration (0.1 mg.  $\text{CrO}_3$  per cu. metre of air) even in the most favourable conditions so far tried and forced ventilation must be retained.

The use of chromium plate to reduce the wear of cylinders of internal combustion engines continues with favourable results.<sup>27,28</sup> An analysis of the causes of wear of Diesel engine cylinders suggests that chromium will reduce all types of wear except that due to distortion; an increase in life of 200–1000% is claimed and, in addition, piston and piston-ring wear is reduced by up to 75%.<sup>27</sup> This paper includes an account of the Van der Horst process as applied to Diesel engine cylinders; this process involves anodic treatment of the electro-deposited chromium in the chromic acid plating solution to produce a fissured network whereby lubricant can be retained; cathodic treatment of the chromium plate for a short time in certain acid solutions (*e.g.*, phosphoric acid) has also been claimed to be effective in producing such a network, the size of the plateaux being controllable during deposition by suitable adjustment of the sulphate ratio, temperature, and current density, and after deposition by heat-treatment of the deposit before etching.<sup>29</sup>

It is well known that chromium plating tends to reduce the resistance of steel (especially hard steel) to repeated stresses and that caution must be used in applying chromium plating to highly stressed parts; an example of the coincidence of a fatigue crack in steel and a crack in chromium plate has been illustrated.<sup>30</sup> On the other hand, it has been reported from Germany that chromium plating can improve the fatigue strength of certain aluminium alloys.<sup>31</sup>

In a comprehensive investigation of the properties of electro-deposited chromium,<sup>32</sup> deposits were produced with Vickers diamond hardness numbers between 310 and nearly 1000; the physical properties (hardness, density, Young's modulus, tensile strength, electrical resistivity), which differed widely in the metal as deposited, approached common values after heating to 1200°; the properties of the softest deposits were little changed by this heat-treatment. Hard deposits had a high oxygen content (*e.g.*, 0.4%) and increased in density on heating with the formation of cracks. Stress per unit area of cross section decreased with increase

of thickness of deposit (except with soft deposits) because of the formation of cracks. This outstanding research provides the most complete picture of the properties of electro-deposited chromium which has so far been drawn. Other investigations have given useful information bearing on the mechanism of chromium-plating and on the structure of the deposit; results of X-ray analysis have indicated that chromium is deposited as an unstable hydride of hexagonal or body-centred structure whose decomposition leads to stresses and cracks in the coating (this investigation also deals extensively with the theory of chromium plating).<sup>33</sup> Investigators have long suspected hydrogen of being responsible for some of the abnormal properties of electro-deposited chromium and that its removal at a suitable rate might result in sounder and more adherent coatings; the general question of the gas content of chromium, its effect on the lattice and methods for its removal have been examined in America,<sup>34</sup> whilst in Germany, the results of work on the hardness and gas content of chromium have been published.<sup>35,36</sup> The adhesion of chromium deposits is difficult to assess because of the extreme brittleness of the deposit; interesting results have been obtained by means of a shear adhesion test<sup>37</sup>; the best figures were obtained with thin deposits on hard steel: too high a current-density was detrimental and the repeated application of a roller to the deposit reduced the shear adhesion considerably (this result perhaps explains the flaking in practice of some chromium deposits under the action of repeated heavy stresses).

Operating details and plant have been described for the production of electrolytic chromium containing 98.8% Cr on a pilot plant scale of 50–70 lbs. per day; a sulphate electrolyte was used with anodes of lead containing 1% of silver; a yield of 1 lb. of chromium per 5 kw. hr. was obtained.<sup>38</sup>

*Cobalt.*—In a further report on methods of electrowinning of cobalt from cobaltic ores, a method of large scale operation is recommended based on development trials on a pilot plant scale of about 5 lbs. of cobalt per day: an estimate is also given for the construction and operating costs of a plant having a daily capacity of two tons of cobalt metal, the total costs being estimated at 34.4 cents per lb. of cobalt. The recommended process is similar to one previously described and referred to in last year's Report: it involves roasting the ore and leaching it with sulphuric acid, removing the impurities and precipitating cobalt carbonate which is added to the electrolytic cell containing a solution of cobalt sulphate and insoluble anodes; the solution is operated at 60° with stainless steel cathodes. At a cathodic current density of 24 amp. per sq. ft., the cathode efficiency was 84% and 2.0 kw. hr. of electrical energy were expended per lb. of cobalt produced.<sup>39</sup>

*Copper.*—An examination of the suitability of fluoroborate solutions for electro-depositing copper has indicated that a higher limiting current density is usable compared with sulphate solutions; throwing power is similar in the two baths but the fluoroborate solution is not suitable for use in lead-lined tanks.<sup>40</sup> Copper-plating is extensively used for preventing casehardening, thus enabling it to be localised to desired areas, but reliable information on the thickness needed under given conditions of case-hardening is not generally known; for cementation at 1000°,

producing a hardened layer 1–2 mm. thick on unprotected areas, a copper coating of at least 0.02 mm. (preferably 0.03–0.04 mm.) is recommended.<sup>41</sup> Copper powder was produced at the Norddeutsche Raffinerie, Hamburg, by the electrolysis of sulphate solutions without additions, the sponge being dislodged from the cathode every half hour by hammering; the cells were emptied every 4–5 days, the slurry being washed, dried and screened.<sup>42</sup>

*Lead.*—The life of the aluminium-bronze rotor of a high-speed fuel pump for gas turbine engines is considerably prolonged by electro-plating it with lead to a thickness of 0.0004 in., followed by a thin coating of tin, which is diffused into the lead by heating in oil; indium was not found sufficiently superior to tin to justify the extra cost.<sup>43</sup> It has been suggested elsewhere that tin is superior to indium in preventing the corrosion of lead bearings by oil. Lead coatings are used to protect steel from corrosion as well as from wear, and for these applications methods of testing the thickness of the coating are needed; the jet-test has been found satisfactory using a corroding solution of acetic acid and hydrogen peroxide.<sup>44</sup>

Fluoroborate and fluorosilicate solutions have long been used with satisfactory results for lead plating and refining and attempts to find alternative solutions which are easier to control and are free from industrial hazard have been unsuccessful until the introduction of the lead sulphamate bath. This bath has now been reported to have been successfully used in Italy for lead refining in a multiple cascade system;<sup>45</sup> the solution contained 80 g. of lead and 100 g. of free sulphamic acid per litre: a current density of 10–12 amp. per sq. ft. with a voltage of 0.5 were used; 135 kw. hr. were expended for each metric ton of lead produced. Trials have been made with various sulphonic acids as a basis for lead plating and refining solutions with mixed results. An ethyl benzenesulphonate was reported to be unsuitable<sup>46</sup>; a *p*-toluene sulphonate solution with glue and aloin as addition agents was considered to be suitable for refining but its poor throwing power compared with the usual solutions may make it unsuitable for plating.<sup>47</sup> Russian investigators have concluded that phenol sulphonate or benzene disulphonate solutions with gelatine as addition agent are suitable for use either for refining or for electro-plating.<sup>48</sup> Fluorosilicate solutions were used for refining lead in Japan during the war; the process was operated on a comparatively small scale and did not have any unusual features of importance.<sup>49</sup>

*Manganese.*—Laboratory investigation at the U.S. Bureau of Mines has shown that a chloride solution can be used in place of the more usual sulphate solution for the electrolytic extraction of manganese. The chloride electrolyte has the advantages of lower cell voltage and greater feed recovery (i.e., a smaller plant for solution preparation) but the disadvantages of a more corrosive solution, the necessity for ventilation to remove anode fumes and the loss of nitrogen at the anode, involving constant replacement of ammonia. The solution is operated at a current density of 45 amp. per sq. ft. and a cathode efficiency of 70%; the recovered manganese assays more than 99% Mn.<sup>50</sup> Further data on the treatment of domestic ores by the sulphate process originated by the U.S. Bureau of Mines has been reported;<sup>51</sup> this process is said to owe its

successful development from the laboratory to the commercial stage to the work of the Electrolytic Manganese Corporation whose process at Knoxville has been described.<sup>52</sup> A similar sulphate process is used in India.<sup>53</sup>

*Magnesium.*—In a new type of electrolytic cell for the electrolysis of fused magnesium chloride, anodes and cathodes were in the form of concentric tubes with an inter-electrode spacing of one inch; the objectives of simple, compact design with low power consumption were achieved in a trial cell rated at 10,000 amp. whose construction and operation have been described in detail.<sup>54</sup> An investigation of the influence of concentration of magnesium chloride in a fused electrolyte showed that maximum cathode efficiency was obtained with 15–20%.<sup>55</sup> Japanese practice in the electrolytic production of magnesium has been described in two reports<sup>56,57</sup>; one-half to two-thirds of the relatively small production (5000–6000 tons per year, peak production) was derived from sea water.

The Dow Chemical Company's process for electroplating metals on magnesium involves the formation of a zinc immersion deposit from an alkaline pyrophosphate solution followed by plating with copper and finally with the desired finish.<sup>58</sup>

*Nickel.*—Improvements in the electrolytic refining of nickel by the International Nickel Company of Canada have resulted from the introduction of chloride into the electrolyte which has enabled the current density to be increased by 25%, the cathode efficiency to be improved and the cost of removing impurities from the electrolyte to be reduced. Production is now at the rate of 88,500 tons per year with a yield of 1.25 instead of 1.00 lb. of nickel per kw. hr. The electrolyte, which now contains 60 g. of sodium chloride per litre in addition to nickel sulphate and boric acid, is more corrosive and the success of the project was partly due to the development of an improved corrosion-resistant alloy (containing approximately 23% Ni, 22% Cr, 5% Mo, and 50% Fe) for pumps, filters, and auxiliary equipment used for handling the anolyte during the first stage of purification. A detailed description of the improvements made includes the method of treating the nickel starting sheets to secure strong adhesion of the nickel deposit; it consisted of anodic treatment at low current density in a solution of sulphuric acid containing sodium and cupric chlorides.<sup>59</sup>

Scattered data on the physical properties of electro-deposited nickel (mechanical, electrical, and thermal properties, density, stress, etc.) have been collected as a preliminary to the research project of the American Electro-Platers' Society on the physical properties of electro-deposited metals;<sup>60</sup> additional results of tests of hardness and tensile strength of nickel deposited from various solutions have been published subsequently.<sup>61,62</sup> The porosity of thin, decorative coatings of nickel determines the degree of protection which they afford against corrosion; for practical purposes, gross discontinuities such as are measured by well known chemical tests are a useful indication of service life but, from the fundamental aspect, a new conception of porosity has been introduced<sup>63</sup> as a result of measurements of the rate of leakage of gas through thin, detached films of electro-deposited nickel; this "intrinsic" porosity differs for deposits of different metals and a preliminary result also

suggests that, with nickel, it may increase with time of keeping the deposit, possibly confirming the suggestion made elsewhere<sup>64</sup> that nickel deposits are subject to stress cracking under corrosive conditions. Stress in nickel deposits is also of practical importance in reducing the resistance of the plated part to fatigue and in causing distortion of electroformed articles; it is usually a tensile stress having a magnitude of the order of 10–20 tons per sq. in., but it is absent or is compressive in certain bright nickel deposits. Many other metals are ordinarily deposited in a condition of tensile stress but zinc is a notable exception. The whole subject has been much neglected in the past, but interest has been revived in it and several papers have appeared during the period under review, dealing especially with nickel.<sup>62,64,65,66,67,68</sup>

Further results have been reported on the effect of impurities in nickel solutions on the properties of the deposit; 0.05 g. of copper per litre of nickel depositing solution (Watts bath,  $p_H$  5.2) was found to be objectionable; at lower  $p_H$  the detrimental effect of copper was more pronounced.<sup>69</sup> The presence of copper in nickel deposits has been found to lower their resistance to attack by salt spray; for example, under the conditions given, 0.05 g. of Cu per litre lowered the salt spray resistance to one-half and 0.01 g. per litre lowered it to three-quarters of its normal value.<sup>70</sup> Other metallic impurities in solution in nickel-plating baths may also have a detrimental effect on the appearance or properties of the deposit and superior results are obtained, especially in bright nickel-plating, if their concentration is kept low, for example by continuous electrolysis at low current density in a separate vessel through which the solution is circulated; two accounts of American practice of this type of purification have been given.<sup>71,72</sup> Results of the research referred to in the previous Report on colorimetric methods for determining impurities in nickel solutions have been given for  $SiO_2$ , Na, K, Cd, Zn, Al.<sup>73</sup> *p*-Toluene sulphonamide, a brightening and stress-reducing addition agent for nickel-plating solutions, can be estimated to a reported accuracy of 2% by a process of chlorination followed by iodimetric estimation of the extracted compound.<sup>74</sup>

Methods of ensuring that adequate protection is afforded by nickel deposits against corrosion are becoming more widely known and specifications more generally adopted; examples of American specifications for aircraft and automotive industries have been published.<sup>75,76</sup> Known methods of testing the thickness of nickel deposits by magnetic<sup>77</sup> or jet methods<sup>78</sup> continue to be developed and their validity and utility supported.<sup>79</sup>

**Rhodium.**—The high hardness, good reflectivity for light, high melting point and resistance to oxidation and tarnish of electroplated rhodium render it a valuable finish for applications where these properties are important, for example, electrical contacts, reflectors, etc. Some laboratory-test results on the effect of exposure to corrosive environment on the reflectivity of rhodium plated reflectors have been given<sup>80</sup> and its general properties and various engineering and other applications have been described.<sup>81,82</sup>

**Silver.**—Silver-plated steel is claimed to have potential uses in jet or turbine engines; a drawback of this material when exposed to high

temperatures is its tendency to blistering which has been found to be due to the formation of water vapour by interaction between oxygen diffusing inwards and hydrogen diffusing outwards; preliminary heating in nitrogen was found to prevent blistering on subsequent heating in air.<sup>83</sup> Electrolytic processes used in the extraction and refining of silver have been described.<sup>84</sup>

*Thorium and Uranium.*—A method for the electrolytic production of powdered thorium or uranium on a commercial scale, developed by the Westinghouse Corporation,<sup>85</sup> consists in electrolysis of a fused electrolyte using a molybdenum cathode. The deposit forms as a sponge which is protected from oxidation on removal from the cell by the adherent layer of molten salt; the salt can be removed by solution in water and the sponge is then broken up, washed and dried *in vacuo*. The electrolytes were prepared by addition of (a) potassium thorium fluoride to a mixture of equal parts of sodium and potassium chlorides, and (b) uranium tetrafluoride, prepared by hydrofluorination of the oxide, to a mixture of sodium and calcium chlorides.

*Tin.*—The Ferrostan process for the continuous electro-tinning of steel strip to make tin-plate is now operating at the Ebbw Vale works of Richard Thomas and Baldwin Ltd. The process has been described in two publications issued during the period under review.<sup>86,87</sup> The normal method of tin-plating in sodium stannate solution is dependent for its success on maintaining the anodes in a filmed or semi-passive condition in which the tin dissolves entirely as stannate; the current density required for the formation and maintenance of the film is influenced by the alkalinity of the solution and by the presence of anions such as carbonate, acetate, chloride, silicate.<sup>88</sup> Japanese practice in electrolytic refining of tin using a fluorosilicate electrolyte has been reviewed<sup>89</sup>; the maximum production was of the order of 250 tons per month.

*Zinc.*—Zinc dust has been produced in Germany by the electrolysis of sodium zincate solution using nickel anodes and water-cooled cathodes made of elektron-alloy or iron.<sup>90</sup> Japanese practice in the electrolytic production of zinc was to use the Tainton process; the plants had a relatively small capacity, e.g., 35 tons daily.<sup>91</sup>

In a symposium of four papers<sup>92</sup> on the plating of zinc-base die castings, factors controlling the production of sound castings were discussed and the treatment recommended for porous castings was to polish heavily; the castings are first plated with copper and the thickness of this coating should exceed the amount which normally diffuses into the zinc, the recommended figure being 0.0002–0.0003 in. The combined thickness of copper and nickel should be at least 0.001 in.

*Alloy deposition.*—Copper-tin alloys of the composition of speculum metal (45% tin) are being electro-deposited commercially as a decorative coating which has an attractive colour and a good resistance to tarnish; typical applications are to domestic table-ware and to reflectors. A recommended method of deposition using a cyanide-stannate electrolyte, the control of the process and the equipment required have been described,<sup>93</sup> whilst elsewhere, the practical aspects of the process have been discussed from the view-point of the plating shop superintendent.<sup>94</sup> Copper-lead alloy bearings have been electro-deposited from an alkaline

acetate bath containing tartrate or citrate; factors affecting the composition of the deposit were investigated and the possibilities of the process are critically examined.<sup>95</sup>

Tin-zinc alloy plating has been developed and applied in production in this country for the protection of steel against corrosion; it is particularly applicable to components which have to be assembled by soldering. The coating is claimed to be a substitute for cadmium-plating and its various advantages and methods for the control of the process have now been described in America<sup>96</sup>; practical information on the operation and control of the process in this country has also been given.<sup>97</sup>

The electro-deposition of alloys of tungsten with cobalt, nickel and iron has been investigated using a neutral or slightly acid solution containing tartrate and borate.<sup>98</sup> The current efficiencies were low (30% at best) and the coatings were found to be considerably harder than pure tungsten but they were not impervious to liquids. Secondary reduction of tungsten by atomic hydrogen is reported to be encouraged by the presence of a second metal which forms a solid solution with the tungsten, *e.g.*, molybdenum.<sup>99</sup> Cobalt-molybdenum and iron-molybdenum alloys are claimed to be deposited from a strongly alkaline solution containing glucose; the molybdenum is said to be deposited by atomic hydrogen with which the first formed layers of cobalt or iron are saturated since no molybdenum is obtained from such solutions in the absence of these deposits on the cathode.<sup>100</sup> Work on the alkaline citrate solution which was used in the exhaustive study of the deposition of alloys of tungsten with iron group metals, referred to in the last Report, has been extended by other investigators to determine the best conditions for depositing alloys of tungsten with cobalt<sup>101</sup> and iron<sup>102</sup> containing 50% of tungsten; this work was confined to determining the effect of changes in concentration of the constituents of the solution,  $p_H$ , temperature and current density upon current efficiency and composition of deposit.

*Electrolytic-polishing.*—The process of electrolytic-polishing of metals has, with a few notable industrial exceptions, been chiefly used so far for the polishing of specimens in preparation for micro-examination or for the study of the mechanism of the process and the properties of the resulting surface. Its potentialities for the industrial finishing of metals appear on the whole to be in an early stage of development although stainless steel and aluminium have been treated on a production scale for several years. Methods for the electrolytic-polishing of stainless steels have been reviewed together with other methods of finishing these materials.<sup>103</sup> Trials on an industrial scale of two methods of electro-polishing stainless steel—orthophosphoric/sulphuric acid and orthophosphoric acid/glycerine—have enabled practical details to be recommended; for polishing stainless steel cutlery, a variant of the phosphoric acid/glycerine method is recommended in which an anodic current density of 4.5 instead of 0.5–1.0 amp. per sq. in. is used in a solution containing a slightly higher concentration of phosphoric acid.<sup>104</sup> The electro-polishing of nickel in sulphuric acid solution gives rise to practical difficulties owing to saturation of the solution with nickel sulphate; solutions developed at the Battelle Memorial Institute which are claimed to work continuously by deposition of nickel on the cathode, contain a

mixture of phosphoric and sulphuric acids with or without a small addition of chloride.<sup>105</sup> A Japanese method of electro-polishing tungsten contacts using a cold, 10% solution of sodium hydroxide resulted in superior performance both in arc extinction and low contact resistance.<sup>106</sup>

Techniques for electro-polishing metals for micro-examination have been described for various steels (using perchloric-acetic acid solution)<sup>107</sup> and for silver (using a cyanide solution).<sup>108</sup> A perchloric acid-ethanol solution is said to be useful for electro-polishing a wide variety of metals in preparation for micro-examination.<sup>109</sup>

The best conditions for electro-polishing metals can be forecast more clearly and accurately if current-voltage (C-V) data are used to plot  $\frac{V}{C}$  against V instead of C against V.<sup>110</sup> The chemical activity of aluminium which has been freshly electro-polished under suitable conditions has previously been shown to be greater than after it has been exposed to the air; this work has now been extended to zinc and iron whose true physico-chemical properties can be revealed in this way.<sup>111</sup> Electron-diffraction studies of copper after electro-polishing in phosphoric acid solution failed to reveal any oxide film,<sup>112</sup> giving further evidence of the possibility of producing metal surfaces free from oxide; results of other electron-diffraction work on electro-polished surfaces has been reviewed elsewhere.<sup>113</sup>

### Miscellaneous

*Preparation for electroplating.*—In a new technique for cleaning metals, known as multi-phase cleaning, a bath is used with two liquid layers—an organic solvent on top and an emulsion of organic solvent and water below; this method is said to be more efficient and quicker than ordinary methods and to have been used commercially with success.<sup>114</sup> The sodium hydride process, which is being widely used to remove scale from steel (especially stainless steel) and non-ferrous metals, involves immersion in molten sodium hydroxide containing a small concentration of sodium hydride (2%) continuously maintained by a generator; a plant for treating sheet steel at the Lukens Steel Co., said to be the largest in the world, has been described,<sup>115</sup> and the principles of the use of the process for wire and strip<sup>116</sup> and non-ferrous metals<sup>117</sup> have been discussed. European practice in the electrolytic removal of scale has been reviewed.<sup>118</sup>

The decorative electro-plating of accessories of toys and model railways involves a series of operations which must all be performed by bulk treatment in barrels; a description has been given of the processes involved—de-burring, barrel polishing, degreasing, bright dipping and barrel plating.<sup>119</sup>

*Electro-deposition processes.*—Photographs and photomicrographs have been published in support of the claim that periodic reversal of the current during electro-deposition of copper from cyanide and sulphate baths results in smoother deposits and more rapid plating.<sup>120</sup>

Various applications of electro-forming continue to be described. A full account of the development work undertaken to produce satisfactory moulds for plastics and die-casting showed the various stages in the

evolution of an improved method of producing thick deposits of low stress which would withstand both plastic compression moulding and pressure die-casting in zinc or in metals of lower melting point; a nickel-cobalt deposit produced from a bath containing fluoride, boric acid, sodium naphthalene tri-sulphonate and cadmium was found to be successful for a number of applications.<sup>121</sup> Electro-forming has been used as a method of producing small articles such as fountain pen caps which are required to have precise dimensions or properties not easily attainable by ordinary production methods; a description of an installation for making 40,000 such articles per week illustrates the potentialities of the process for this type of work.<sup>122</sup> Precision work for optical purposes is another example; descriptions have been given of the production of small concave mirrors which differed from the glass master form by only about  $5\ \mu$  per cm. along the diameter,<sup>123</sup> concave copper replica gratings,<sup>124</sup> precision prisms in copper,<sup>125</sup> and reproducible surface finish standards with roughness values of 1–1000  $\mu$ /in.<sup>126</sup> Graphite is sometimes favoured for metallising non-conductors in preparation for electro-forming and its merits for this purpose and the factors which affect its performance have been discussed.<sup>127</sup> For the metallising of plastics, a reduced film of silver from an ammoniacal solution is frequently used; a copper film reduced from Fehling's solution by a special reducing agent (not clearly defined) is said to give better results.<sup>128</sup> The literature on electro-forming has been reviewed with special reference to the properties of deposits which are of interest for electro-forming (Ni, Co, Fe, Cu, Ag).<sup>129</sup> The presence of ferric iron or chloride in copper sulphate solutions used for electro-forming are amongst the causes of rough deposits.<sup>130</sup>

A special plating machine is used at the G.E.C. works at Philadelphia for the localised deposition of silver contact rings, 0.0005 in. thick, around bolt holes on copper bus bars; use of this machine superseded the fixing of rings by a thermal process; the machine is semi-automatically controlled and a high rate of solution flow over the cathode surface results in a rate of deposition some 200 times as rapid as ordinary tank deposition.<sup>131</sup> Careful planning of electroplating shops can have an important and lasting effect on the efficient operation of the shop; vats should be correctly grouped and their size, especially depth, can have an important effect on output; methods of making and draining floors are also important. These and other aspects of the lay-out of plating shops have been discussed in two papers.<sup>132,133</sup> Efficient filtration is essential in the modern plating shop to maintain the quality and speed of plating; answers to a questionnaire by 18 large plating firms provide a useful picture of American experience and practice.<sup>134</sup>

### Electrochemical processes

The electrolytic production of fluorine in Germany was referred to in the last Report; a further statement about this industry is available. The low temperature cells at Leverkusen ( $75^\circ$ : KF. 2.5 HF) and the high temperature cell at Falkenhagen ( $245^\circ$ : KF. HF) are described; each type used 2000 amp. per cell, the low temperature cell operating at a lower anode current density and a higher efficiency than the high temperature cells.<sup>135</sup>

Cuprous oxide may be produced with colloidal properties by electrolysis and the product is a better fungicide than material made chemically; the process and equipment are simple and the process can be modified to give copper oxychloride by the use of a supplementary carbon anode at which chlorine is evolved.<sup>136</sup>

Graphite anodes are used almost universally in America for the electrolytic production of chlorates. The rate of attack on such anodes is considerably affected by the chloride concentration and temperature, being most pronounced in dilute chloride solutions at high temperatures; low anode current density also promotes increased attack on the anode. Internal oxidation of the graphite is attributed to chemical action of hypochlorous acid. Graphite treated by impregnation with oil, wax or resin is approximately twice as resistant to attack as untreated graphite but changes in conditions of electrolysis affect the degree of attack similarly.<sup>137</sup>

### Primary and secondary cells

*Primary cells.*—The efficiency of a number of organic inhibitors of zinc corrosion in the Leclanché cell has been compared with that of mercury and chromate films, but the expectation that the successful inhibitors would be found to be useful additions to the dry-cell electrolyte was not realised, although gliadin and mesonin which are inhibitive constituents of the paste wall of the cell increased the capacity to some degree.<sup>138</sup> Modifications in the construction of a Leclanché dry-cell, consisting in the use of a thin spun paste partition layer and of a depolarising mix of finely-ground artificial  $\text{MnO}_2$ , mixed with a high proportion of acetylene black, resulted in an increase of one-third of the normal short circuit-ampere; this is a useful increase for special cells such as are needed for photo-flash lamps.<sup>139</sup>  $p_H$  measurements and analyses during heavy continuous discharge of a Leclanché cell have shown that the depolarising action starts in the middle and inner portion of the depolariser adjacent to the carbon electrode but that, as discharge proceeds, the outer layers become reduced to a greater extent than the remainder.<sup>140</sup> Neutralisation of the electrolyte of a Leclanché cell during discharge can be beneficial if it is done with ammonia but harmful if done with a solution of oxides of calcium, zinc or magnesium.<sup>141</sup>

Heavy duty cells depolarised with chlorine can be constructed to have a high capacity at moderate rate of drain (e.g., 6 amp. per sq. ft.) or a heavy discharge rate of 75–150 amp. per sq. ft. for a few minutes.<sup>142</sup> A study of the mechanism of reduction of oxygen at the air depolarised electrode has shown that the mechanism is different according to whether the electrolyte is acid or alkaline; in acid solution reduction of oxygen to hydrogen peroxide is irreversible at carbon electrodes.<sup>143</sup> A new thermo-electric cell has been described consisting of silver and aluminium electrodes wrapped in asbestos impregnated with a potassium salt; this cell is said to give a steady p.d. of 0.1–0.2 volts without corrosion at constant temperatures higher than 400°.<sup>144</sup>

An authoritative review of new types of primary cell, of dry cells for use at sub-zero temperatures and of the operating characteristics of lead secondary cells has been made.<sup>145</sup> The improvements in the life

of dry cells which have been made as a result of research and development are reflected in the revised American standard specifications for dry cells.<sup>146</sup>

*Secondary cells.*—Grids of lead storage batteries are normally made of a lead alloy because the physical properties of pure lead and the difficulty of casting make it generally unsuitable for the purpose. A low discharge type of cell with pure lead grids was found to lose capacity very slowly (e.g., at the rate of about 15% in the first year) whereas the same design of cell with grids made of 12% Sb alloy lost all of its capacity in the first year; the rate of self discharge was appreciably accelerated with only 0.5% Sb.<sup>147</sup> Alloying additions may also have a marked influence on the resistance of positive grids to anodic corrosion; silver, for example, has been found to be very beneficial whilst zinc, magnesium, copper and antimony were all very harmful and arsenic, iron and bismuth had only a slight effect in the concentrations studied.<sup>148</sup> Negative plates lose capacity much more rapidly than positive plates, but the functioning of the negative plate can be improved by various additions which are made for the purposes either of increasing the mechanical strength of the plate, increasing the porosity of the active material, stabilising its gel structure or preventing its oxidation, or of encouraging the deposition of lead sulphate away from the sponge lead particles of the plate. The general question of addition agents and expanders for negative plates has been extensively reviewed with 248 references (223 of them to patents),<sup>149</sup> whilst elsewhere the influence of expanders on the discharge characteristics, with special reference to sulphation has been examined,<sup>150</sup> and the subject of materials for lead accumulator plates has been discussed in a series of papers.<sup>151</sup>

All miners' lamps used in Germany are fitted with the alkaline type of secondary cell and have a long trouble-free life; details of their manufacture in various factories have been given.<sup>152</sup>

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# ACIDS, ALKALIS AND SALTS

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WHILE developments are reported on new chemicals, the firmly established and traditional products of the heavy chemical industry still continue to receive the most attention. This is evidenced by the numerous publications of work on ammonium compounds, nitrates, phosphatic fertilisers, sulphuric acid, chlorine, caustic soda and lime. During the war large plants were erected for the production of magnesium from sea-water, but during the year there have been a fair number of references to work on dolomite showing that this continues to be an important source for magnesium compounds. Magnesium compounds in general have been the subject of considerable work during the year.

Gaseous oxygen is receiving increased attention as its cheaper production widens its application. Evidence of this interest, in both production and use, was shown by the good attendance at a conference which was held in February, 1948, on developments in the industrial production and use of gaseous oxygen, arranged jointly by the Institution of Chemical Engineers and the Physical Society. As a source of oxygen and energy, and as a powerful oxidising agent, hydrogen peroxide of high strength has also attracted a fair amount of attention.

The problem of recovering alumina from clay continues to be the subject of considerable study. Much development work is still being done on the production of the rutile modification of titanium dioxide; there is very little new work being reported on anatase.

The electrical industry has had to enter the chemical field for the production of di-electric and luminescent materials as indicated by the large number of patented processes taken out by electrical companies for the manufacture of these materials.

This year has seen the conclusion of the publication of details of the German chemical industry and it will be interesting in the near future to see how the dissemination of hitherto secret information affects world developments.

## Ammonia and ammonium salts

The continuing interest in the growing demand for nitrogenous fertilisers is reflected in the publication of a number of reviews. L. F. Audrieth<sup>1</sup> gives a review of trends in nitrogen chemistry with special reference to derivatives of  $\text{NH}_3$  analogous to those of  $\text{H}_2\text{O}$ . P. Cuillaumeron<sup>2</sup> describes the production of synthetic ammonia in the U.S.A. and Canada during the war. At the end of the war, the U.S. production of aqueous ammonia was 3,500 tons per day, and that of Canada 500 tons per day. A general survey of the production of synthetic ammonia is given in an unsigned article in *Chemical Engineering*.<sup>3</sup> In 1947, the U.S. production of synthetic ammonia was 1,430,000 tons. The article includes a list of

the principal producers with the daily production capacity of the different plants. Special reference is made to two new factors brought to this field by the Government war factories, namely production from cheap natural gas instead of coke and the use of ammonium nitrate as a fertiliser. Allocations for the Marshall Plan are estimated to leave a domestic shortage in the U.S. of the equivalent of 500–600 tons  $\text{NH}_3$  per day. Ammonia, fertilisers and nitric acid production at I.G. Farbenindustrie, Leuna, are described in a C.I.O.S. report<sup>4</sup> edited by R. Holroyd. The ammonia synthesis plants were conventional and old fashioned, producing about 1200 tons  $\text{NH}_3$  per day. Ammonium sulphate was made by the anhydrite process. Nitric acid was made at 5 atmospheres with platinum (+5%) of rhodium gauze. The manufacture of concentrated nitric acid, ammonium nitrate, mixtures of ammonium sulphate and ammonium nitrate, and calcium nitrate are described.

The recovery of ammonia from ammonium sulphite waste liquor is described by A. E. Markham, Q. P. Peniston and J. L. McCarthy.<sup>5</sup> The waste liquor after pulping hemlock chips in ammonium bisulphite solution is concentrated and converted into a brittle black solid which can be crushed for pyrolysis at a temperature of not less than 600° c. to give a recovery of over 90% of the nitrogen content of the solids as ammonia.

During the year under review there has not been much reference to ammonium sulphate. A process is described<sup>6</sup> for the continuous neutralisation, of ammonium sulphate, vacuum filtration and subsequent drying in a steam-heated drier.

#### *Nitric acid and nitrates*

In the catalytic oxidation of ammonia to nitrous oxide, the effects of temperature, space velocity, ammonia concentration and time of operation have been studied by K. A. Kobe and P. D. Hosman,<sup>7</sup> using a mixture of oxides of manganese and bismuth as catalyst. With oxygen a maximum yield of 71% was obtained at 200° c., with space velocity of 5–6 ml. of gas per ml. of catalyst per minute, and a concentration of 10–11%  $\text{NH}_3$ . With air the conversion was 10% lower. The activity of the catalyst falls off rapidly after about 40 hours and it cannot be regenerated by heating. A process is claimed by the Wisconsin Alumni Research Foundation<sup>8</sup> for the production of nitric oxide from air with or without added oxygen. The gases are preheated to 1970° c., and then to 2200° c. to form nitric oxide and the resultant mixture is forced through a cooling bed where the gases are cooled to below the decomposition temperature of nitric oxide in less than one-tenth of a second. The preheating and chilling zones comprise beds of refractory such as alumina, zirconia, zircon, or spinel where the surface area of the bed is not less than 22 sq. ft. per cu. ft. of volume.

A modified Kachkaroff–Matignon lead chamber process for the simultaneous production of sulphuric and nitric acid is described by F. Salsas–Serra<sup>9</sup> based on experience gained at Vado, Italy. Hot nitrous fumes are rapidly cooled with condensed steam to give 1–4% nitric acid;  $\text{N}_2\text{O}_4$  is converted to about 55% nitric acid in the first nitric absorption stage, residual nitrous fumes are absorbed in 75–95% sulphuric acid in presence of  $\text{SO}_2$  which is maintained in slight excess throughout the

system; the  $\text{N}_2\text{O}_4$  from denitration is liquefied and treated separately with oxygen and dilute nitric acid to produce concentrated nitric acid.

On the subject of ammonium nitrate crystallisation, P. Miller and W. C. Saeman<sup>10</sup> describe with some detail, the working and modification of the Oslo-Krystal system of rapid circulation through a bed of growing crystals to give a satisfactory crystal form and size. J. D. Biggs<sup>11</sup> claims a modification of the standard Hobler tower for the production of ammonium nitrate to give nearly double the output. The consolidated Mining and Smelting Co., of Canada claim<sup>12</sup> a process for the production of ammonium nitrate granules from solution using a spray tower.

The explosions of ammonium nitrate fertiliser on board two steam ships at Texas City in April 1947, described in the previous year's report, are the subject of an official report by the United States Bureau of Mines (G. M. Kintz, G. W. Jones and C. B. Carpenter<sup>13</sup>). This suggests that the fertiliser, containing 95% ammonium nitrate, was ignited in the hold of s.s. *Grandcamp* during stowage probably through illicit smoking of tobacco. The detonation is then stated to have been due to heat and pressure produced by steam which was blown into the hold, after sealing it in an attempt to smother the fire. Another contributory factor to detonation was the contact of the ammonium nitrate with the combustible paper bags and paper dunnage. The secondary explosion of s.s. *High Flyer*, resulting from material projected by the detonation of the *Grandcamp*, was aggravated by the fact that this contained in adjacent holds, sulphur and ammonium nitrate fertilisers. Rules for the handling and transport of ammonium nitrate fertiliser are proposed by a committee representing interested organisations. M. A. Elliot<sup>14</sup> has carried out experiments on the exothermal decomposition of mixtures containing ammonium nitrate. Ammonium nitrate when pure and unconfined does not undergo exothermic reaction below  $250^\circ$  but the presence of metal, for example, zinc, reduces the temperature of reaction.

Large-scale production of free cyanamide,  $\text{NH}_2\text{CN}$ , from nitric acid and calcium cyanamide is described by A. J. Courtier.<sup>15</sup> The preparation of hydroxylamine by the electrolytic reduction of nitric acid in sulphuric acid at a mercury cathode is discussed by G. Lazzari with particular reference to current density and agitation of the mixture.<sup>16</sup> In the formation of nitrogen trichloride, by passing chlorine gas over a solid ammonium salt, the use of an inert carrier containing one or more substances capable of reacting with the hydrochloric acid or other acids produced, is claimed by W. S. Hutchinson.<sup>17</sup> The removal of nitric acid from a non-aqueous reaction system by adsorption on sodium fluoride or other fluorides is claimed by Stein, Hall & Co. Inc.<sup>18</sup> A mixture of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}$ , which remains liquid at low temperatures, is claimed by du Pont de Nemours & Co. as an oxygen supplier.<sup>19</sup>

## Phosphates

Under the subject of minerals for chemical and allied industries, S. J. Johnstone<sup>20</sup> gives a review of phosphorus-containing minerals and discusses phosphatic fertilisers, the manufacture of phosphoric acid, and the use of phosphates in food manufacture, in the textile industry, etc.

A description has been published of the mining and processing of Florida phosphate.<sup>21</sup>

A fertiliser containing 19.5% available  $P_2O_5$  out of a total 21.0%  $P_2O_5$  has been obtained on a pilot plant by arc-furnace fusion of olivine and phosphate rock, reported by R. W. Moulton.<sup>22</sup> The operation and control of a unit producing 30-35 tons of concentrated superphosphate per hour by a continuous-mixing process is described in some detail by G. L. Bridger, R. A. Wilson and R. B. Burt.<sup>23</sup> The disadvantages of the batch-mixing process are obviated by mixing the reactants in a funnel type mixer (without any moving parts), effecting the mixing by the turbulence of the feeds. The mixture drops on to a rubber belt conveyor where it sets to a solid mass which is broken up by a disintegrator at the discharge end.

The manufacture of phosphorus at Piesteritz, Germany, has been described by A. H. Loveless.<sup>24</sup> Most of this material had been published in B.I.O.S. reports to which reference was made in a previous Annual Report (1946).

Work on the rate of oxidation of red phosphorus has been carried out by M. S. Silverstein, G. F. Nordbloom, C. W. Dittrich and J. J. Jakaboin.<sup>25</sup> They point out that the undesirable characteristics of commercial red phosphorus, namely the spontaneous combustion, generation of poisonous phosphine, hygroscopicity, etc. result from, and increase with, the rate of oxidation. They have found that this rate of oxidation is increased considerably by the presence of copper, bismuth, silver, iron, or nickel; cadmium and tin produce a moderate increase, while lead and chromium have little effect. Aluminium and zinc decrease the rate of oxidation. Taking the compounds of these metals, the best inhibitors are the hydroxides, aluminium hydroxide being the best. Since commercial red phosphorus contains about 250 p.p.m. of iron and 30 p.p.m. of copper, these being mainly on the surface, the phosphorus can be treated with 5% sulphuric acid to remove the iron and with 5% sodium cyanide solution containing 1.5% sodium hydroxide for the removal of the copper. This will reduce the iron figure to the order of 5 p.p.m., and copper to 3 p.p.m. Alumina treatment may be carried out by adding 10% sodium bicarbonate solution to the red phosphorus, followed by the equivalent quantity of aluminium sulphate. The amount of aluminium hydroxide recommended is 0.5-7%. The working of a pilot plant for the production of red phosphorus by a continuous process is described by P. Miller, R. A. Wilson and J. R. Tusson.<sup>26</sup> Molten white phosphorus is fed continuously into a stainless steel reactor and heated to near its boiling point (280° c.) with constant stirring. The slurry from the reactor, containing about 40% of red phosphorus, is subjected to a stream of carbon monoxide heated to 288° c. in an upwardly-inclined, screw conveyor-vaporiser from which the white phosphorus is distilled off, condensed and re-cycled.

The production statistics for tetra sodium pyrophosphate from 1936 to 1947 and of phosphoric acid from 1939 to 1947 are given by J. R. Skeen,<sup>27</sup> who also tabulates the uses of the sodium salt. The partial hydration of anhydrous tetra sodium pyrophosphate is claimed, by A. G. Aitchinson (Westvaco Chlorine Products Corp.<sup>28</sup>), to give a free

flowing, readily soluble product useful as a detergent, wetting agent or emulsifying agent. Although the product only contains about half as much water (the patent specification claims 15–30%) as does  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ , its rate of dissolution is stated to be the same as that of the decahydrate and twice that of the anhydrous salt. The effect of heating mono calcium phosphate (anhydrous or with  $1\text{H}_2\text{O}$ ) at various temperatures and for various periods in steam or air has been studied by W. L. Hill, S. B. Hendricks, E. J. Fox and J. G. Cady.<sup>29</sup> They give a comparison of the products obtained from commercial and pure samples of mono calcium orthophosphate and calcium acid pyrophosphate.

### Sulphur and sulphuric acid

The preparation of colloidal sulphur by heating ammonium polysulphide with an aldehyde in the presence of a protective colloid such as casein or alginate is claimed by F. F. Schwartz.<sup>30</sup>

Problems involved in handling liquid  $\text{SO}_2$  have been discussed.<sup>31</sup> The production of sulphurous acid for conditioning flotation pulp at the treatment plant of Lake George Mines in New South Wales, is described by P. D. Fisher.<sup>32</sup> The sulphur is burned on a sloping reverberatory hearth, completing the combustion in two chambers. The sulphur dioxide is scrubbed from the gases by passing them through five superimposed beds of coke, each 1 ft. thick, in a vertical tower through which water passes from a fine spray. The sulphurous acid obtained from the tower contains about 3%  $\text{SO}_2$ .

A. N. Rao<sup>33</sup> discusses the economics of sulphuric acid manufacture in India. The high price of sulphuric acid produced in India is stated to be due chiefly to the cost of imported sulphur and to the age and uneconomic size of the majority of the plants which operate the chamber process.

The recovery during the war, from crushed colliery refuse, of pyrites averaging 42% sulphur, is reported<sup>34</sup>; the peak production was 25,000 tons of pyrites per year. This was blended with imported ore for burning in Herreshoff furnaces. A process for the production of sulphur from pyrites at the Orkla Works, Orkanger, Norway, has been described.<sup>35</sup> From Sweden comes a report of the flash roasting of fine pyritic flotation concentrates.<sup>36</sup>

Three methods have been described for the filtration of molten sulphur<sup>37</sup>: (1) steam-jacketed Kelly filters with stainless steel filter cloth and a pre-coat of filter aid, one-sixteenth to one-eighth in. thick; (2) Niagara filters with leaves, frames, etc., of 316 stainless steel, into which a mixture of molten sulphur and diatomaceous earth is pumped, the latter acting as filter aid; and (3) Adams filters in which porous carbon tubes are mounted vertically in a steam-jacketed shell. J. F. McVey (F. W. Berk & Co.),<sup>38</sup> claims a process for the preparation of sulphur for burning by mixing sulphur with an alkali or alkaline earth oxide, hydroxide, carbonate, bicarbonate, or borate, *e.g.*, 1–2% sodium bicarbonate. E. C. Bierce<sup>39</sup> describes a sulphur smelter of shaft furnace type in which a controlled volume of combustion air and gases is drawn through and out of the ore-bed.

The chamber process for the manufacture of sulphuric acid is meeting

with more competition from the contact process, but with the need to use indigenous raw material, there is still a large number of chambers in the country. It is therefore of interest to read W. H. Dyson's historical review<sup>40</sup> of the process. He points out the need for increased attention to burners to give a high  $\text{SO}_2$  content in the gas with little or no dust, adequate  $\text{NH}_3$  oxidation systems to provide excess of  $\text{NO}_2$  when required, the elimination of stoppages by avoiding mechanical breakdowns by duplication of pumps and fans, increased use of scientific instruments and the employment of operatives with wider chemical knowledge. The electro-filtration of roaster gases from burning pyrites is discussed by A. G. Ondovilla.<sup>41</sup> The three stages of dust separation in electro-filtration are illustrated: first natural sedimentation, then the electro-filtration in which the greater part of the dust is removed and the final stage in which the ionisation resulting from the electro-filtration causes most of the remaining dust to separate. As a secondary reaction  $\text{NO}_2$  is produced, but the amount is only about 1% of the total amount of nitric acid required in the lead chamber process, and it is therefore not economic to collect.

Continued interest in platinum catalysts for the oxidation of sulphur dioxide to sulphur trioxide is shown in claims for a catalyst comprising a support, *e.g.*, alumina, silica, or magnesium sulphate on alumina on which is deposited a thin layer of precious metal containing platinum (90–50) and palladium (10–50).<sup>42</sup> In another case the support is coated with a solution of platinum metal compounds in an organic solvent of low volatility; the whole is then heated to remove the solvent and leave the platinum metal catalyst on the surface of the support.<sup>43</sup>

A cyclic process for the manufacture of sulphuric acid at Trail, B.C., is described by A. F. Snowball.<sup>44</sup> An obsolete 35-ton-per-day plant was redesigned for a cyclic process involving the use of pure sulphur dioxide and pure oxygen and gave a final production of 200 tons of 100% sulphuric acid per day with 99.5% efficiency. The circulating gas stream was maintained at 25% sulphur dioxide and 30% oxygen, using pure sulphur dioxide from the acidification of ammonium bisulphite (obtained by absorption of roaster gases in ammonia solution) and pure oxygen obtained by electrolysis. Conversion into sulphur trioxide was effected over vanadium catalyst at 600° C.

Concentration of sulphuric acid under vacuum is described by J. F. Burke and E. Mantius,<sup>45</sup> with special reference to materials of construction. Recent developments include impregnated graphite, Hastelloy D (Ni 85, Si 10, Cu + Mn 5%), and tantalum for the tubes. Recent improvements in the drum type sulphuric acid concentrator are discussed by J. H. Berger and A. J. Gloster,<sup>46</sup> with special reference to corrosion difficulties, gasket materials, mechanical failure of high-silicon iron pipes, fume nuisance, and corrosion in Cottrell precipitators due to overloading and the use of sulphuric acid containing nitric acid. The du Pont falling-film process for sulphuric acid concentration is described by F. S. Chambers and R. F. Peterson<sup>47</sup>: 67–69% sulphuric acid is pre-heated to about 150° C. in steam-jacketed tubes and flashed into a vessel at 25 mm. pressure, giving a concentration to about 72.5%. This acid is then concentrated to 92–93% by allowing it to flow as a film down

the inside of steam-heated tubes at 100–150° c., still at 25 mm. pressure. The plant is constructed mainly of high-silicon iron. The falling-film tubes are occasionally flushed with hot water to remove deposited iron and lead salts.

The thermal decomposition of sulphuric acid is effected by injecting the spray from a rotating cup into a furnace, with or without the use of compressed air.<sup>48</sup> Sulphur trioxide may be stabilised and its melting point lowered by the addition of 2–15% by weight of thionyl chloride.<sup>49</sup> A dehydrating agent such as  $P_2O_5$  may also be present.

Hydrogen sulphide in coal gas is catalytically oxidised to sulphur and water by passing it with oxygen over nickel or cobalt sulphide at a temperature of not more than 80° c. but not less than the dew-point of the gas. The catalyst is regenerated by treatment with a solvent for sulphur recovery, for example, ammonium sulphide.<sup>50</sup> A laboratory investigation is described of a method for utilising waste hydrogen sulphide and sulphur dioxide by converting them to sodium thiosulphate.<sup>51</sup> The best yield, 95–96%, was obtained with equimolecular amounts of sodium sulphite and sodium bisulphite at 20–40° c.

Carbon disulphide is produced by passing a mixture of gaseous hydrocarbons and sulphur vapour over a catalyst such as activated bauxite at 450–750° c. The product contains hydrogen sulphide, hydrogen, excess sulphur and unchanged hydrocarbon as well as the carbon disulphide. The sulphur is removed by cooling, the hydrogen sulphide is removed by treatment with aqueous sulphur dioxide, and the  $H_2S$  free gases are cooled to condense the carbon disulphide which is purified by distillation.<sup>52</sup> The theoretical reaction in the formation of carbon disulphide from sulphur dioxide and anthracite is discussed by C. W. Siller.<sup>53</sup> He describes experimental furnaces for batch and continuous operation. The effect of such factors as furnace temperature, sulphur dioxide flow-rate, size and grading of coal, and type of carbonaceous material are described. A yield of about 90% of carbon disulphide is possible on thermodynamic grounds; yields up to 80% were actually obtained. The process appears to take place in three stages: (1)  $SO_2$  and C react in the lower part of the furnace to give COS and  $CO_2$ ; (2) the COS dissociates into carbon monoxide and sulphur in the hot middle section; (3) the atomic sulphur formed in stage (2) reacts with the anthracite to give carbon disulphide. It is thus important to have a hot middle section in the furnace, e.g., 1250° c.

## Halogens

### *Fluorine and fluorine compounds*

The progress made in the preparation of fluorine has been reviewed by R. W. Porter.<sup>54</sup> Fluorine can be produced commercially by the electrolysis of a mixture of anhydrous hydrogen fluoride and potassium fluoride in cells, with carbon anodes and steel cathodes, charged initially with potassium hydrogen fluoride and hydrogen fluoride. The composition of the electrolyte is maintained constant by the continuous addition of anhydrous hydrofluoric acid. The operating temperature is 105–110° c. Special precautions are necessary when handling fluorine, particularly

under high pressure; half-inch steel barriers should be used and the plant operated by remote control.

According to M. P. Matuszak<sup>55</sup> concentrated or anhydrous hydrofluoric acid can be recovered from an azeotropic mixture of water and hydrogen fluoride by dissolving about 35–40 mol. % of potassium fluoride in the mixture and then separating the constituents by successive steps in a three-stage distillation. This recovery process is based on a discovery that, when an alkali fluoride is dissolved in a liquid, beyond a critical salt concentration, the vapour pressure of the aqueous solution is greater than that of the hydrogen fluoride solution and increases progressively with increasing salt concentration until the two solutions have widely different boiling points. The alkali-metal fluoride must be in liquid solution through all the stages of distillation. Potassium fluoride is the salt preferred on account of cheapness, availability and optimum stability in combination with the hydrogen fluoride. In a patented process<sup>56</sup> for the removal of hydrogen fluoride from non-aqueous fluids, the porous pellet of sodium fluoride used is prepared by the thermal decomposition of sodium hydrogen fluoride. Pellets are regenerated in the same way as they are produced, by heating in a current of gas at 300–500° C. In order to ensure perfect removal of the hydrogen fluoride, a train of absorbers is employed ending with refrigeration towers at a temperature of –80° C. B. F. Hartman,<sup>57</sup> in a patented process for hydrogen fluoride recovery, scrubs gases containing hydrogen fluoride with fluorosulphonic acid and then heats the absorbent to recover the hydrogen fluoride. C. C. Peavy and J. Happel<sup>58</sup> describe a process for the recovery of hydrogen fluoride, which has been used as a catalyst in hydrocarbon reactions, by scrubbing the gaseous mixture with sulphuric acid and then stripping the enriched acid.

In a patented process<sup>59</sup> for the manufacture of the double fluoride of aluminium and sodium, calcium fluoride is heated with concentrated sulphuric acid and the gases are collected in water. The resulting solution of hydrogen fluoride and fluosilicic acid is treated with silica to convert the hydrogen fluoride into fluosilicic acid, which is precipitated as the sodium salt by the addition of sodium chloride. The precipitate is collected, washed and suspended in water (100–200 g. per litre) at 80° C. The required amount of hydrated wet alumina is added (55%  $\text{Al}_2\text{O}_3$ ) and the mixture is kept at 80° C. for about six hours. The heavy precipitate of  $3\text{NaF} \cdot 2\text{AlF}_3$  is settled and the silica suspension siphoned off. The precipitate is then treated with a little hydrofluoric acid to remove the entrained silica.

### *Chlorine*

J. J. Graham<sup>60</sup> has described in detail a mercury cell plant producing  $5\frac{1}{2}$  tons of caustic soda and nearly 5 tons of chlorine per 24 hours, together with equipment for the manufacture of calcium hypochlorite. R. K. Lumie and R. B. MacMullin<sup>61</sup> have reviewed the rapid growth of chlorine plants in the U.S.A. By the end of 1948, chlorine production was expected to reach nearly 5000 tons per day, 75% of this being used in the preparation of other chemicals mainly organic. J. E. Vivian and R. P. Whitney<sup>62</sup> describe work on the absorption of chlorine by water

in a Raschig ring-packed tower. A modified mass transfer coefficient, based on molecular chlorine concentration, is calculated. S. P. Sen<sup>63</sup> describes the utilisation of waste chlorine after liquefying it for transportation. R. B. MacMullin<sup>64</sup> discusses the diaphragm-cell versus the amalgam cell for chlorine/caustic production. The capital cost of the amalgam cell per unit of output is slightly higher and the running costs are slightly less than those of the diaphragm-cell. The former is more suitable for producing potassium and lithium hydroxides, sodium metal, sodium sulphide, and for some organic reductions. Further developments of the rotating cathode and falling-film types of mercury cell are discussed. According to A. Antoniani<sup>65</sup> washing out impurities from sodium chloride by water is successful commercially for the purification of the electrolyte in the operation of the mercury cathode cell.

The preparation of synthetic hydrogen chloride from hydrogen and chlorine is described by A. H. Maude.<sup>66</sup> The most satisfactory type of burner is made of water-jacketed steel and the resulting gas is air-cooled in long iron pipes. If aqueous hydrochloric acid is required, submerged combustion can be used to give the solution directly. The burner is made from graphite tubes and burns in a rubber-lined steel tank with an inner brick shell. Acid from the tank is circulated through a Karbate cooler. A. Antoniani<sup>67</sup> has calculated the dew-point of the gaseous mixture obtained in the industrial synthesis of hydrochloric acid from electrolytic chlorine and hydrogen. The temperature at which a liquid phase separates on cooling the gas depends primarily on the water concentration, which is itself a function of the oxygen content of the electrolytic chlorine used, as well as of the humidity of the initial hydrogen and chlorine. Allowance must be made for the fact that the condensed phase is aqueous hydrochloric acid and not pure water. The method of calculation is demonstrated and a table is given covering the range in which the chlorine is of 69–90 vol. % purity. The gases are either perfectly dry initially or are saturated with water vapour at 5° or 35° c. A. Lippman, jun., and R. L. Comstock<sup>68</sup> describe the manufacture of hydrogen chloride in conjunction with that of sodium or potassium sulphate. Sulphur dioxide, excess air and steam are introduced at the base of an insulated tower meeting a cloud of alkali chloride particles suitably injected at points higher up. Ferric chloride in the salt make possible a reaction temperature of 805° c. instead of 845° c. After cooling to 205–370° c., hydrochloric acid is recovered from the cleaned gases. According to W. S. Allen,<sup>69</sup> in the manufacture of chemically pure hydrochloric acid, free chlorine may be removed from the chlorine-water vapour (HCl gas-free) by supplying carbon monoxide to the stream. The free chlorine is reduced to hydrochloric acid and the carbon monoxide is oxidised to carbon dioxide. Activated carbon serves as a catalyst for the reaction at a temperature of not less than 350° F. J. W. Latchum,<sup>70</sup> in a patented process for the recovery of hydrogen chloride in the butane isomerisation process, describes how the hydrochloric acid is recovered by liquefying the gaseous mixture and separating the liquid into two phases, a hydrocarbon phase and a hydrogen chloride phase.

In a patented process<sup>71</sup> for the manufacture of calcium hypochlorite, basic calcium hypochlorite is neutralised with aqueous hypochlorous acid

to form  $\text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$ . Preferably neutralisation is carried out in the presence of  $\text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$ .

G. A. Petroe<sup>72</sup> describes a patented process for the production of chlorine dioxide by interacting a chlorine-air mixture with a chlorite. The chlorine and air streams are automatically controlled so that the air content of the chlorine dioxide-air mixture never falls below the safe amount. In another patented process<sup>73</sup> for the production of chlorine dioxide, a solid alkali or alkaline-earth chlorite is allowed to react with nitrogen dioxide (diluted with air), carbon dioxide and water vapour or gaseous hydrochloric acid diluted with air. In a further patent<sup>74</sup> chlorine dioxide, free from chlorine and suitably diluted with air, is produced by treating an alkali chlorate with nitrogen dioxide containing the necessary amount of diluent. The generation and evolution of chlorine dioxide by an acid from a solution of an alkali or alkaline-earth chlorite is repressed by the addition of hydrogen peroxide or a salt which will yield hydrogen peroxide.<sup>75</sup> The amount of hydrogen peroxide is such that the ratio of  $\text{H}_2\text{O}_2$  (as 100 vol) : chlorite (as available chlorine) is not greater than 4 : 1.

N. C. White<sup>76</sup> discusses the factors influencing the efficiency and economy of the electrolytic production of chlorates from chlorides. The design and operation of an American plant, producing potassium chlorate from potassium chloride, are described with a diagrammatic flow-sheet. M. James<sup>77</sup> has investigated the influence of a number of factors on the rate of attack of graphite anodes during the electrolysis of sodium chloride solutions to chlorate. The anode attack is increased by rise in temperature and by decrease in sodium chloride concentration. Chemical oxidation by hypochlorous acid may be largely responsible for the internal attack on the graphite. The rate of attack increases approximately linearly with the reciprocal of anode current-density. Graphite treated with oil, wax or resin is about twice as resistant to attack as the untreated material. J. C. Schumacher<sup>78</sup> describes the electrolytic production of sodium chlorate and of sodium and potassium perchlorate with details of the design and efficiency of the cells, together with reference to corrosion problems and the design of the crystallisers. J. C. Schumacher has also<sup>79</sup> described the electrolytic cells for two American alkali perchlorate plants. The cells consist of a mild steel cathode, a synthetic stone cover and perforated platinum sheet anodes. The aqueous sodium chlorate electrolyte flows through the cells, arranged in series, the voltage drop across each cell being 6.8. The platinum loss is about 0.2 ounces troy per ton of sodium perchlorate produced. A commercial plant for the electrolytic production of potassium perchlorate is also described in some detail by C. A. Hampel and P. W. Leppla.<sup>80</sup> The authors give full details of the electrolyte composition (sodium chloride and chlorate), temperature and electrical conditions, together with data on the further treatment of the solution on leaving the cell, and the precipitation of potassium perchlorate by means of potassium chloride. The mother liquor of sodium chloride is concentrated and returned to the feed tank for re-electrolysing to chlorate and thence to perchlorate.

According to A. Urion and G. Lejeune<sup>81</sup> ammonia can be satisfactorily removed from aqueous brine ( $\text{NaCl}$ ) by the passage of a current of air.

W. T. Anderson<sup>83</sup> reviews the development of the technique of chlorination photosensitisation and of the means for producing the necessary light. A simple new type of glass reaction vessel for gas-liquid reaction is described in which the light is supplied by a tubular mercury-quartz arc.

A patented process<sup>83</sup> for the purification of anhydrous liquid halides of Group IV metals utilises 0.05–0.5% of a heavy metal soap and then passes a stream of hydrogen sulphide into the liquid. The impurities are adsorbed and co-precipitated with the metal sulphides. Another process<sup>84</sup> for the purification of anhydrous liquid halides of metals of Group IV utilises a cold treatment with sulphur followed by heating under reflux with sulphur, preferably in the presence of chlorine and a heavy-metal soap, and finally distilling. Alternatively, the halide may be treated in the vapour-phase with solid, liquid or gaseous sulphur halides and then distilled. F. K. McTaggard<sup>85</sup> describes the treatment of graphite with chlorine (1–2 lb. chlorine per lb. of graphite) at 1250–1450° c. in a silica-tube furnace giving products containing 0.5 or 0.05% ash.

### *Bromine*

P. Hart<sup>86</sup> describes equipment for sulphur dioxide control in sea-water bromine plants utilising automatic sampling, titrating and electrical measuring instruments. According to a patented process,<sup>87</sup> silicon tetrabromide is manufactured by treating ferrosilicon (200-mesh) with bromine vapour at a temperature of about 150° c. The excess bromine is boiled off and no hydrogen is used.

### **Alkali metal compounds**

The occurrence and world production of sodium chloride, sodium carbonate and sodium sulphate have been reviewed by S. J. Johnstone.<sup>88</sup> Their principal uses are described and the standard specifications for sodium chloride for various purposes are discussed. R. Schauder<sup>89</sup> has discussed the manufacture of salt in South Africa together with some of the scientific and economic problems. R. L. Comstock<sup>90</sup> has patented a method for purifying brine in which chemical agents, which inhibit the solubility of impurities or precipitate undesirable ions, are dissolved in the water before the crude salt is added. The Mathieson Alkali Works<sup>91</sup> have patented a method for the electrolysis of aqueous sodium chloride using a mercury cathode. The anodes and anode cover are formed from a single piece of graphite, the anodes being in the form of fins or tips. Electrical connection is made on the top of the cover so that the metallic connections are maintained out of contact with the chlorine. A U.S. patent by A. F. Holden<sup>92</sup> describes a rectifier for chloride salt baths comprising, for example, H<sub>3</sub>BO<sub>3</sub> 30–70, TiO<sub>2</sub> 10–40, SiO<sub>2</sub> 2–15, and KCl 2–15 pts. The purpose of such a rectifier is to reduce the alkalinity of the bath and remove metallic oxides and decomposed salts.

In a patented process by K. E. Long and H. W. Cromer<sup>93</sup> a porous absorbent sodium fluoride pellet is prepared by heating a pressed pellet of sodium hydrogen fluoride at 300–500° c. to drive off the hydrogen fluoride. This pellet is then employed to absorb hydrogen fluoride from fluids or gases at 85–125° c. The pellet is mechanically strong and may

be repeatedly regenerated without damage. If absorption takes place at a temperature of less than  $85^{\circ}\text{C}$ ., swelling, disintegration and even liquefaction may occur if the quantity of hydrogen fluoride absorbed is too great.

D. R. Torgeson<sup>94</sup> has given corrected values for the heats of formation and decomposition of natural trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) of 99.9% purity as well as for two samples of artificial trona. The heats of formation, decomposition and solution are  $-7,760 \pm 20$ ,  $44,260 \pm 100$ , and  $6,219 \pm 4$  g.-cal. per mol. of trona.

W. Reinders and H. W. Nicolai<sup>95</sup> give details of a cyclic procedure now being operated in which sodium bicarbonate is precipitated at  $35^{\circ}\text{C}$ . and the solution cooled to  $10^{\circ}\text{C}$ . and treated with sodium chloride and ammonia to precipitate pure ammonium chloride and leave a suitable mother liquor for recycling to the first stage. Ammonium chloride can thus be recovered from the mother liquor of the Solvay process; equilibrium diagrams are given.

W. R. Carruthers<sup>96</sup> has patented an apparatus for the manufacture of salt cake by reaction between sulphuric acid and sodium chloride with improved efficiency. The Comptoir des Textiles Artificiels S.A.R.L.<sup>97</sup> have taken out two patents for the purification and electrolysis of sodium sulphate. In the first of these heavy metals and alkaline earths are removed from the sodium sulphate solution by the addition of trisodium phosphate and sodium sulphide, followed by filtration and centrifuging. In the second patent, the purified sodium sulphate solution is electrolysed, using a purified mercury cathode, to give aqueous sodium hydroxide and to regenerate mercury for return to the bath. The anolyte is continuously circulated to produce a solution containing not less than 250 g. of sulphuric acid per litre. The electrolysis is carried out at  $40^{\circ}\text{C}$ . and 6 volts with a current density of 6 amps. per sq. dm. using lead anodes containing 12–15% of antimony. L. G. Goldenberg<sup>98</sup> believes that the suspension method is the most satisfactory one for drying impure sodium sulphate for glass making and describes such a plant. According to C. J. Nyman and T. D. O'Brien<sup>99</sup> sodium sulphate, intimately mixed with 0.4% of iron or 1% of copper sulphate, is completely reduced to sodium sulphide at  $600^{\circ}\text{C}$ . by hydrogen. An 80% reduction is obtained under the same conditions with methane at  $850^{\circ}\text{C}$ . Ammonia and hydrogen sulphide are not as efficient as hydrogen. Sodium sulphide and sodium sulphate form a eutectic, at  $665^{\circ}\text{C}$ ., containing 43% of sodium sulphide. With gas reduction therefore the temperature should be less than  $650^{\circ}\text{C}$ . to avoid liquefaction of the charge and consequent retardation of the reaction.

E. S. Tomula<sup>100</sup> describes the decomposition of potassium feldspar. The feldspar is pelleted, with manganese chloride as catalyst, at  $105\text{--}110^{\circ}\text{C}$ . and the pellets are heated at  $680\text{--}700^{\circ}\text{C}$ . for 6 hours in a stream of air saturated with water vapour. The product loses about 40% of the chlorine and can be used as a fertiliser as it contains 81.7% of water-soluble potassium. A patented method<sup>101</sup> for the preparation of potassium hydroxide compositions, claims the distillation of potassium hydroxide solution with an inert water-immiscible liquid of b.p. lower than  $100^{\circ}\text{C}$ ., e.g. acetals, mono- or di-ethers, while vigorously agitating. The

water is then separated and the liquid returned to the distillation vessel, until all the water has been removed. The mixture is then cooled and stirred giving a suspension of finely divided potassium hydroxide in the water-immiscible liquid.

I. E. Muskat and F. D. Ayres<sup>102</sup> have patented a method for the purification of alkali hydroxide solutions in which the aqueous hydroxide solution, containing silica, is heated with liquid ammonia at 50–70° C. under a pressure sufficient to keep the ammonia liquid. Two layers are formed, the heavier of which contains the silica. The upper layer is separated and more contaminated alkali hydroxide is added until the two phases again separate, when the upper layer is again separated to yield the pure alkali hydroxide. In another patent by A. E. Muskat,<sup>103</sup> metal vessels are rendered resistant to alkali hydroxide solutions, greater than 50% strength, by coating them with a mixture of polystyrene and benzene-soluble ethyl cellulose. The coating is hardened by treatment with aqueous alkali hydroxide at temperatures above 66° C. The coating is preferably applied as a solution in suitable organic solvents.

According to G. L. Cunningham<sup>104</sup> anhydrous alkali metal sulphides, in granular form, are produced by treating polysulphides with alkali metal amalgam containing, for example, 0.1–0.3 wt. % of metal in anhydrous ethyl alcohol at about 50° C. Part of the product is heated with sulphur to form fresh polysulphides and the mercury is used to prepare fresh amalgam. Exclusion of air from the alcoholic solution prevents oxidation of the sulphides while slight excess of amalgam prevents formation of mercuric sulphide. The formation of ethoxide is retarded by having a non-conducting container and clean sulphur. Selenides and tellurides may be made in a similar manner.

### Alkaline earth compounds

The operation of a modern limestone quarry has been described by D. J. Isaacs<sup>105</sup> with details of the mechanisation and illustrations of the machinery. O. Bowles and N. C. Jenson of the U.S. Bureau of Mines<sup>106</sup> have tabulated the quantities of limestone sold and used annually in the U.S.A. from 1921 to 1945. In 1945 the production exceeded  $151.7 \times 10^6$  tons. Although lime-burning has been practised for so long, the subject still attracts considerable attention and there have been numerous references to it during the year. The form and number of lining blocks for a lime kiln have been calculated by W. Regner.<sup>107</sup> Full details are given for the mensuration of the shapes required for a kiln 36 ft. high by 9 ft. maximum external diameter. Regner also provides calculations for the size of kiln required to provide for the clarification of juice from a given through-put of beet. This assumes a 36-hour roasting of the limestone. W. R. Cliffe<sup>108</sup> discusses rotary lime kiln practice in its various aspects and concludes that the rotary kiln yields a more uniform product than the vertical type, the sole advantage of which is its lower initial cost. The lime manufacturing process has also been discussed by V. J. Azbe<sup>109</sup> with reference to the operation of both rotary and vertical kilns. Combustion in the lime kiln has been dealt with by J. Watt.<sup>110</sup> It is possible to calculate the general and thermal efficiencies of a lime kiln from the

composition of the exhaust gases, ratio of fuel fed to lime produced, calorific value and chemical analysis of the fuel, and the percentage of  $\text{CO}_2$  in the limestone. General equations derived from the data enabled two sets of curves to be constructed giving combustion conditions in the kiln. The use of these curves by the kiln operator should improve the fuel efficiency, output and quality of the lime. W. B. Lenhart and N. C. Rockwood<sup>111</sup> have given a full account of the "fluo-solids" process for making a high grade "soft" burnt lime. Cold, graded limestone is fed into the top of a vertical reactor where the finely divided solids are kept in suspension in air or other gas at a temperature greater than  $600^\circ\text{C}$ ., this being the ignition temperature of the injected fuel oil. The fuel oil thus burns on and around the particles of limestone ensuring optimum thermal conditions. The calcined and cooled product is withdrawn continuously from the base of the reactor. This reactor has pre-heated burning and cooling zones suitably proportioned and separated. The burning zone is kept at a temperature of about  $930^\circ\text{C}$ . The operation of the reactor is accurately controlled by means of recording pyrometers and manometers. The dust losses in the process average 5–10%. About 42 gallons of fuel oil are used per ton of lime produced.

W. C. Hansen and E. E. Pressler<sup>112</sup> have determined the solubilities of slaked lime and gypsum in dilute sodium and potassium hydroxide solutions at  $25$  and  $30^\circ\text{C}$ . at alkali concentrations up to 0.25 mols. per litre. The solubility curves are used for estimating the degree of super-saturation of the liquid phase of Portland cement pastes.

Limestone is used extensively to neutralise waste acids. A. L. Reid<sup>113</sup> describes the neutralisation of a waste acid from a plating works by passing it upwards through two beds of limestone, while part of the neutralised effluent is pumped back to an eductor, which raises the crude effluent from the preliminary settling tanks and simultaneously dilutes it. This obviates pumping the acid, while channelling of the beds or coating of the limestone with calcium sulphate is avoided. H. L. Jacobs<sup>114</sup> points out that limestone is normally preferred for neutralising waste acids but it cannot be adapted to  $p_{\text{H}}$  control and it reacts slowly owing to its high magnesium content. It is of value however when sufficient reaction volume is available, *e.g.*, in neutralising sulphuric acid in concentrations greater than 0.5%. In other cases slaked lime should be used.

T. Heilmann<sup>115</sup> gives a method for concentrating calcium carbonate by froth flotation. Low grade limestone ore, containing, for example, 64%  $\text{CaCO}_3$ , is subjected to froth flotation in the presence of a collector consisting of a  $\text{C}_{10-14}$  fatty acid, a derivative thereof containing a  $\text{CO}_2\text{H}$  group, and either a  $:\text{SO}_4$  or  $:\text{SO}_3\text{H}$  group attached to a carbon atom in the chain, or an alkali-metal soap of any of these acids. The calcium carbonate concentrate is mixed with the crude ore to give a product containing 77%  $\text{CaCO}_3$  for use in making cement. Precipitated calcium carbonate is generally manufactured from calcium chloride and sodium carbonate. Such a process is described by R. L. Taylor<sup>116</sup>; specially lined or stainless steel or bronze equipment is used and the temperature, rate of addition and  $p_{\text{H}}$  have an important effect on the resulting particle size of the precipitate. The precipitated calcium carbonate is used for paper coating, extending titanium pigments, in rubber and plastics,

and in pharmaceuticals. E. M. Allen<sup>117</sup> gives a process for producing a pure finely-divided calcium carbonate for dentifrices or pigments by agitating impure calcium sulphate with an excess of aqueous sodium carbonate and removing the heavy crystals of the resulting hydrated double carbonate by filtration. The product is purified by suspension in sodium carbonate solution through which gas is bubbled and the froth is decomposed with hot water. The sodium sulphate and carbonate from the filtrate can be recovered.

A basic calcium chlorate, which is useful as a weedkiller, is manufactured by introducing calcium hydroxide into an aqueous solution of calcium chlorate at 50–100° C., thus precipitating the basic chlorate  $\text{Ca}(\text{ClO}_3)_2 \cdot \text{Ca}(\text{OH})_2$ .<sup>118</sup>

The production of strontium carbonate from Indian celestite is described by M. Prasad and G. V. Dange.<sup>119</sup> The strontium carbonate is precipitated from the strontium sulphate with sodium carbonate and the effect of temperature, agitation, particle size and other factors on the reaction are given.

The principal barium mineral is barytes and its production in the United States is described by A. C. Harding.<sup>120</sup> In 1945 U.S. production reached 696,062 tons. The greater part of this was ground for use in oil-well drilling muds. The next biggest user was the lithopone industry, followed by barium chemicals. In order to produce other barium compounds from barytes it is generally first reduced to barium sulphide. Thus C. I. Cox<sup>121</sup> describes the production of barium nitrate from barytes by first reducing the ground mineral with coke at 900–950° C. in an externally-heated rotary chromium steel muffle furnace. After the barium sulphide has been ground in a ball mill and extracted with water it is boiled with sodium carbonate to precipitate barium carbonate. The barium carbonate is dissolved in nitric acid to give the barium nitrate with a 60% yield. Another method for obtaining a water-soluble barium salt from barytes is described by G. P. Kane, N. R. Kuloor, and M. S. Varde.<sup>122</sup> The barium sulphide, obtained from barytes or its solution is added to 10% aqueous magnesium chloride solution and the mixture raised to the boil. Barium chloride is formed with magnesium hydroxide and sulphur as by-products. Solid barium sulphide gives a more gelatinous precipitate of magnesium hydroxide while the addition of turkey-red oil increases the settling rate. D. E. Nagy and B. C. Redmon<sup>123</sup> give a method for making barium dicyanimide by treating the zinc salt with barium hydroxide solution. The zinc hydroxide is filtered off and the filtrate is neutralised with hydrochloric acid and evaporated *in vacuo*. The barium dicyanimide is not hygroscopic. Calcium or copper dicyanimides can be used in place of the zinc compound. K. H. Butler<sup>124</sup> describes how lead-activated barium silicates emit blue and blue-green lights when excited by radiation of 2537Å. The energy output of these new phosphors is comparable with that of tungstates, while the colours obtained are more saturated. Other references to luminiscent barium compounds are given in the section on luminescents. Barium cyanide, according to a recent patent,<sup>125</sup> is made by treating barium hydroxide monohydrate with hydrocyanic acid at 32° C. If

barium hydroxide or monoxide are used, sufficient water must be added to form the monohydrate.

The mineral dolomite is still an important source of magnesium compounds. A recent patent<sup>126</sup> describes how the dolomite is calcined with 1.07 parts of silica for every one part of lime to form inert calcium silicate. The magnesia may then be easily separated by mechanical or chemical means and the carbon dioxide evolved can be recovered. If steam is present calcination at 850° C. is effective; otherwise the temperature should reach 1000° C. Another method of treating dolomite is described in a British patent.<sup>127</sup> The calcined dolomite is suspended in aqueous ammonium sulphide and the mixture is steam-heated until the ammonia is completely liberated. The unattacked magnesium oxide and hydroxide are filtered from the resultant calcium sulphide solution which is evaporated to dryness to yield solid calcium pentasulphide for use in insecticides. Another recent development in this field is to pass a slurry of calcined dolomite through a series of carbonating tanks in which  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  is formed as mechanically separable crystals.<sup>128</sup> The  $p_{\text{H}}$ , controlled by the supply of carbon dioxide, is reduced in stages from 12.5 to 8, while the temperature is raised from 25° to 36° C. The resultant magnesium carbonate hydrate and calcium carbonate are separated by a method dependent on their different densities, *e.g.*, centrifugal separation or froth flotation. L. G. Weinrub<sup>129</sup> describes kilns for dead-burning magnesite and gives the advantages and disadvantages of heating shaft kilns by oil, gas and solid fuels. Magnesite for bricks should be dead-burnt in kilns heated by oil or gas, while coal should be used only if containing a very low ash. Weinrub concludes that, although rotary kilns are less economical than shaft kilns, they have several advantages such as mechanisation and the possibility of a higher temperature, *i.e.*, 1700° C. instead of 1600° C. The production of magnesia from sea-water is described.<sup>130</sup> The sea-water is treated with a small amount of calcium hydroxide, clarified and magnesium hydroxide is precipitated with more calcium hydroxide. The precipitate is washed free from chlorides and converted into basic magnesium carbonate with carbon dioxide. This basic carbonate may be calcined to give light magnesia. Heavy magnesia can be obtained by calcining pure dry magnesium hydroxide at 550–1100° C. Another process for producing magnesium oxide is described in a recent patent<sup>131</sup> where magnesium oxide of high reactivity is manufactured by heating magnesium carbonate or hydroxide with a uniform grain size of less than 0.1 mm. at 800–1100° C. for 0.1–120 secs. Y. Letort and L. Halm<sup>132</sup> have made a detailed study of the effect of calcination on crystal growth of magnesia. In general, the size of the magnesium oxide crystal increases with the rise of calcining temperature but impurities and the use of a reducing atmosphere also tend to increase the crystal size. The origin of the magnesia is without influence. The crystal size is important in the manufacture of Sorrel cements since too large a size results in poor setting. The preparation of a magnesium oxide material for reduction is given by T. W. Vigers.<sup>133</sup> The magnesium oxide slurry is mixed with finely divided carbonaceous reducing material and then de-watered. The resultant mixture is heated at 800° C. in an inert atmosphere to remove free water and then at

800–1250° c. to remove combined water. The production of a magnesium oxide material for reduction purposes is also described by N. Collins, W. W. Mower, and H. Church.<sup>134</sup> An intimate mixture of magnesium hydroxide and a solid reducing agent is achieved by adding the reducing agent to either the hydroxide slurry, or to the brine before the conversion of the magnesium into the hydroxide, but in either case before separation of the hydroxide from the mother liquor. A recent patent<sup>135</sup> describes the production of briquettes of calcined magnesia material by calcining dolomite in a rotary kiln and discharging it into a special cooling chamber in which humid air, water vapour or steam is added to control the absorbed water content at 0.6–0.8%. This material is mixed with a reducing agent such as ferrosilicon and pressed to form hard and dense briquettes. Magnesium carbonate, according to a recent patent,<sup>136</sup> is produced from an aqueous magnesium hydroxide slurry by carbonating at a controlled rate so that the conversion of hydroxide into carbonate is not more than 0.12 mol. per gallon per hour. Crystals of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  with a particle size of less than  $200 \mu$  are produced and are readily separated. A recent method<sup>137</sup> for treating hydrous magnesium carbonate consists of mixing it with not more than 10% of water at 21–43° c. to form a plastic mass which is formed into shapes, dried at less than 100° c. and then fired. If desired, 1–5% of iron oxide, chrome ore, bauxite, silica or a borate, phosphate or silicate of sodium or calcium may be incorporated. Basic Refractories Inc. separate magnesium carbonate from calcium carbonate by calcining the dolomite, grinding and slurring with water.  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  crystals are added as seeds and a gas containing carbon dioxide is bubbled through the slurry.<sup>138</sup> The crystals grow to such size that they can be separated from the calcium carbonate by froth flotation. H. S. Cooper<sup>139</sup> has patented a method of producing anhydrous magnesium chloride by grinding magnesium oxide to 100 mesh, and treating it at 1000° c. with an equimolecular mixture of carbon monoxide and chlorine to form magnesium chloride free from magnesium oxide. Magnesium oxychloride is extensively used for cements and according to a recent patent,<sup>140</sup> hard, dense objects can be moulded in 15–30 secs. from magnesium oxychloride cement at 102–175° c. and 1000–3000 lbs. per sq. in. pressure.

A. Ramuz<sup>141</sup> has reviewed the alkaline earth aluminates and general methods for their production. The conditions for the formation of calcium aluminate are examined and barium and magnesium aluminates are mentioned. R. B. Booth and J. E. Carpenter<sup>142</sup> have patented a method for treating low grade ores of the alkaline earth metals by froth flotation using a water-soluble, sulphonated petroleum hydrocarbon and a fatty acid or its soap as a conditioning agent. Metal Hydrides Inc.<sup>143</sup> have shown that ingots of alkaline earth metals, heated in hydrogen until the reaction starts, yield the metallic hydrides. Heat dissipation and hydrogen flow are so regulated that the heat of reaction maintains the temperature at 300–750° c., thus forming the hydride without fusion of the metal. N. V. S. Knibbs<sup>144</sup> has described the production of alkaline earth oxides from finely divided carbonate by heating in a rotary kiln, after drying, a mixture of the finely divided carbonate, hydrated oxide and water which may be extruded or granulated, but need not be briquetted, before drying.

## Industrial gases

### *Oxygen*

The main use of cheap oxygen gas is in the manufacture of synthetic fuel gases. A modified Fischer-Tropsch process uses oxygen for the partial combustion of natural gas to yield liquid petroleum fuels. The use of oxygen is also being considered for the underground gasification of coal. Oxygen of 98% purity can be produced at a cost of 0.64 kw. hr. per cu. metre and at 0.5 kw. hr. per cu. metre for oxygen of 99.5% purity.<sup>145</sup> O. W. Willcox<sup>146</sup> also emphasises the use of cheap oxygen in the Fischer-Tropsch process and discusses the effect of this cheap oxygen on the technique. The costs of producing oxygen in large and small plants are compared. The applications of oxygen in the German chemical industry has been discussed in a lecture by E. I. Bomshtein.<sup>147</sup> A description has been given by J. T. Hugill<sup>148</sup> of a large-scale oxygen plant producing 100 tons per day. This plant has certain improvements over the older plants and these are emphasised in some detail. In the electrolytic production of oxygen, a recent patent<sup>149</sup> claims the addition of vanadium compounds to an aqueous caustic alkali electrolyte in order to reduce the voltage. In the production of oxygen from air by the separation of gas mixtures, a number of improvements to the Linde process are described in a recent patent.<sup>150</sup> The object of these is to prevent accumulation of high-boiling impurities such as carbon dioxide during the production of liquid oxygen by low temperature air fractionation. In the production of oxygen by two successive expansions of compressed air, accumulation of impurities and grease in the product is avoided, according to a recent patent<sup>151</sup> by removing them as solids after the first expansion. P. M. Schuftan<sup>152</sup> provides a comparative review of modern methods for the production of oxygen of various degrees of purity. The processes for the various qualities of oxygen are given in detail with the power consumption. The possibilities for improving the methods are discussed and methods for producing 40%, 55%, and 80% oxygen are suggested. The use of low pressure systems employing reversing heat exchangers for oxygen production has been discussed.<sup>152</sup> Such units can compete with conventional liquefaction plants and their output can be raised considerably by lowering the standard of purity. For many purposes, the lower purity oxygen is quite acceptable. The problem of heat exchange in the large-scale production of oxygen has been discussed by D. D. Howatt.<sup>154</sup> An alternative system is described giving a power consumption of 0.59 kw. hr. per cubic metre of 100% oxygen. J. A. Weedman and B. F. Dodge<sup>155</sup> experimented with the liquefaction of air in a 2 in. diameter column using different packings and various conditions of working.

Some work has been done on the chemical generation of oxygen. Thus a recent patent<sup>156</sup> describes the manufacture of oxygen-generating candles containing potassium chlorate and barium peroxide, the candles being ignited electrically. Another method is based on the use of chelates which possess the property of absorbing oxygen reversibly with change in physical conditions. The design and operation of a pilot plant utilising this process has been described by B. B. Fogler.<sup>157</sup> In a recent patented

process,<sup>158</sup> oxygen is absorbed by passing air over a contact mass of manganese dioxide, alumina and caustic soda. In another chemical process for the production of oxygen<sup>159</sup> air is passed over a hot solid manganate type of contact mass thereby oxidising it. In both these processes the oxygen is subsequently recovered by passing steam over the contact mass.

M. Ruhemann<sup>160</sup> in reviewing the economics of oxygen production concludes that it can compete with liquid air as the developments in plant design have led to increased efficiency and reduction of losses. D. L. Glizmanenko<sup>161</sup> has reviewed the economics and organisation of the German oxygen industry, while M. K. Sukov<sup>162</sup> has reviewed recent engineering problems in this industry.

### *Other gases*

There have not been many references to gases other than oxygen. H. Boer<sup>163</sup> has described an apparatus for producing ozonised oxygen by electrolysing sulphuric acid using a polished lead anode and a lead cathode, both water-cooled. A review by V. G. Fastovsky<sup>164</sup> of the industrial production of krypton and xenon shows that Soviet processes for these gases closely resemble those of other countries. In the production of solid carbon dioxide a stronger product is obtained by passing the liquid gas into the top of an insulated container fitted with a lid carrying a vent and valve, and out at the bottom to the solidifier.<sup>165</sup> A. T. Grisenthwaite,<sup>166</sup> in reviewing the production and purification of hydrogen by the water-gas catalytic process, concludes that it is now possible to produce hydrogen containing not more than 0.05% of carbon monoxide in a single-stage process, and not more than 0.005% CO in a two-stage process. According to a recent patent<sup>167</sup> nitrogen and hydrogen for ammonia synthesis can be produced by washing a hydrogen-containing gas with liquid nitrogen prior to mixing. The mixture of gas and liquid is used for cooling the gas by heat exchange.

The use of iron oxide for the absorption of hydrogen sulphide is well known and a recent patent<sup>168</sup> proposes to add an aqueous solution of a ferrous salt solution containing a slight excess of ammonium carbonate and bicarbonate. The precipitate obtained is washed and dried to yield  $\alpha$  hydrated ferric oxide in a form particularly suitable for hydrogen sulphide absorption.

### **Miscellaneous**

A comprehensive investigation has been reported on the manufacture of inorganic chemicals at the I.G. Farbenindustrie at Leverkusen.<sup>169</sup> The German processes for making such materials as lithopone, sodium bichromate, hydrofluoric acid, fluorides, sodium sulphide, sulphur compounds, and titanium dioxide are described. Another survey of inorganic chemical production, this time on the Pacific Coast of America, has been made by G. L. Allen.<sup>170</sup> In this case the chemicals are produced mostly from sea water as the raw material and from the salt deposits of Southern California.

In the field of hydrogen compounds B. Orsoni<sup>171</sup> has described a new method for the production of 100% D<sub>2</sub>O from natural water. A new

method for the production of metal hydrides<sup>172</sup> utilises a mixture of an alkaline earth oxide and aluminium which is heated first under vacuum and then at 950° C. The calcium which distils off is condensed and treated with hydrogen to form calcium hydride.

The electrolytic preparation of cuprous oxide offers the advantage of giving a product of specifically colloidal structure and higher fungicidal value and according to V. de Nora and G. E. Sessa<sup>173</sup> it is distinguished by its simplicity and ease of operation. Copper oxychloride may also be produced electrolytically by the partial or total action of chlorine on cuprous oxide, the former being produced at a supplementary carbon anode. Further work on a copper compound has been reported by P. Miller.<sup>174</sup> Details are given of the design, operation and control of a pilot plant producing 600 lbs. copper arsenite per 24 hours. The material was converted from an aqueous suspension to a package product in one operation by using a spray drier. On account of the irritating and toxic effects of the powdered arsenite, the personnel need protection from the product.

A patented process<sup>175</sup> for the manufacture of dihydroxyfluoroboric acid, takes stoichiometric quantities of boric acid, water and gaseous boron trifluoride and heats the mixture to 150° C. for a few minutes to remove excess of boron trifluoride. The dihydroxyfluoroboric acid is obtained with a 97% yield and may be purified by distillation.

Alkali metal selenides can be manufactured by dissolving selenium in an aqueous alkali-metal sulphite solution and subjecting the reaction product to a reducing agent, such as aluminium or zinc, in the presence of sodium or potassium hydroxide. The alkali-metal selenide crystallises out when the reaction mixture is cooled.<sup>176</sup> Metallic selenium itself can be electrodeposited from a solution of selenium oxide in 18 N. sulphuric acid at 100° C. and at a suitable current density.<sup>177</sup> The use of selenium cells is well known and in order to increase the voltage which can be applied across the cell it has been proposed<sup>178</sup> to coat the rectifier disc, which consists of a steel base with an annealed selenium surface, with a lacquer consisting of selenium oxide, cellulose acetate lacquer and a thinner. Improvements in the production of selenium rectifiers are described in three patents.<sup>179,180,181</sup>

Manganese dioxide is used largely for depolarising and in order to produce a suitable grade for this purpose, manganese ores can be roasted to give  $Mn_2O_3$  or  $Mn_2O_4$ . This oxide is then suspended in water and chlorine is bubbled through the suspension yielding manganese dioxide and aqueous manganese chloride. The latter can be used for producing manganese salts or it can be neutralised with lime to give manganese hydroxide which can be treated with chlorine.<sup>182</sup>

Numerous proposals exist for the treatment of waste ferrous sulphate solutions. One such method<sup>183</sup> proposes to neutralise the pickling solution with iron and pass coke-oven gas through it until the  $p_H$  is about 7 to 7.5. It is then further treated with ammonia to a  $p_H$  not less than 8. The precipitate is oxidised to the ferric state by blowing air through the mixture after which the ferric oxide is filtered and calcined to form rouge. The ammonium sulphate solution which is now free from iron can be evaporated or used in a coke works. If the solution is aerated at a  $p_H$

less than 8 only part of the iron is precipitated. In another method<sup>184</sup> for oxidising aqueous ferrous sulphate solution by oxygen, it is proposed to catalyse the reaction by porous carbon. The catalytic activity of the carbon can be increased by heating it under non-oxidising conditions at 925–1000° c. for 5–25 hours.

### *Aluminium*

In the Bayer alumina process, the red muds from the process can be activated for the absorption of hydrogen sulphide by heating red mud in sodium hydroxide solution at 140–190° c.<sup>185</sup> The solubility of alumina in aqueous sodium hydroxide at 60–200° c. has been studied in connection with the Bayer process. At constant temperature, the  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$  ratio decreases with increasing concentration of  $\text{Na}_2\text{O}$  linearly at 100° c. At constant concentration of  $\text{Na}_2\text{O}$  the ratio decreases rapidly with rising temperature up to 100° c., but above 125° c. the ratio decreases slowly with rising temperature. The results show that little advantage in  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$  ratio is gained by extracting with solutions containing more than 200 gms. of  $\text{Na}_2\text{O}$  per litre. A ratio of about 2 : 1 is obtainable during precipitation if the temperature is not less than 125° c. The normal cooling to 100° c. gives a ratio of 1.8 : 1.<sup>186</sup> In a further proposal<sup>187</sup> on the Bayer process, bauxite is heated in a reducing atmosphere at 350–525° c. and then at 200–500° c. in air. The product is then autoclaved with an aqueous alkali solution to give a residue from which magnetic oxides of iron can easily be separated. Such oxides are used for removing hydrogen sulphide from coal gas. Turning to the lime-soda sinter process for the recovery of alumina from kaolin F. J. Cservenyak<sup>188</sup> has described how pelleted mixtures of kaolin, limestone and sodium carbonate are sintered for about 20 mins. at 1320–1350° c. in an oil-fired rotary kiln. The sinter is then ground to 100 mesh and extracted with aqueous sodium carbonate. The liquor is separated by using standard thickeners and the residue is washed and collected on rotary vacuum filters. A high grade alumina can be recovered by known processes. F. J. Frattali, S. J. Green and V. I. McLendon<sup>189</sup> have made an exhaustive study of the system sodium carbonate–sodium sulphate–sodium hydroxide–water, and from this they have devised a method for the recovery of sodium carbonate and sodium sulphate from the effluent liquor in the lime-soda process for alumina production. The liquor is recirculated through the process until the sodium sulphate concentration interferes with the alumina precipitation. It is then necessary to evaporate the liquor at 100° c. and cool it slowly to 23° c. to crystallise out the sodium carbonate which is dehydrated in a rotary drier. When the mother liquor is evaporated at 100° c. it yields a 50/50 sodium carbonate–sodium sulphate mixture which is separated and dissolved in water at 100° c. to form a saturated solution. This saturated solution is treated with lime and the solution is cooled to about 18° c. to crystallise out the sodium sulphate. R. A. Brown, F. J. Cservenyak, R. G. Anderberg, H. J. Kandiner, and F. J. Frattali<sup>190</sup> report that alumina can be recovered satisfactorily from Wyoming anorthosite by the lime-soda-sinter process. It is necessary to sinter the correct proportions of finely ground ore, limestone and sodium carbonate in a rotary kiln at 1350° c. for 25 mins.

The sinter is ground, leached with alkali and filtered off. The leach liquor is freed from silica and the alumina is precipitated by passing a carbon dioxide-air mixture through the liquid. The hydrated alumina is finely calcined to give the anhydrous oxide. The authors have established the optimum conditions for each stage and these must be adhered to. A modification of the Pedersen process has been described by T. T. Hignett.<sup>191</sup> Details are given of a CaO-sinter modification of the Pedersen process for the production of alumina from clay. The extraction of alumina from clays has also received attention from L. Dubrul.<sup>192</sup> The usual process for removing impurities by fusion is not satisfactory with clay and the alumina produced is not pure enough for metallurgical purposes. In discussing the various processes available it is considered that the alkali and thermal reduction methods are inapplicable. Of the acid extraction processes the only suitable ones are those with sulphuric acid or sulphurous acid. In order to obtain pure alumina the lime or CaO-Na<sub>2</sub>O processes are the most satisfactory but the CaO-sinter method is more economical. In the process for the production of alumina from clay using ammonium sulphate, the clay is baked with ammonium sulphate at 400° c. and then leached with water and the alum is purified by crystallisation. Much iron however is extracted simultaneously and builds up in the circulating leach liquor. According to A. T. Sweet and G. D. Gardner<sup>193</sup> this iron is best removed by adding calcined clay during leaching to precipitate the iron as 2NH<sub>3</sub>·3Fe<sub>2</sub>O<sub>3</sub>·5SO<sub>3</sub>. The residues are discarded and this procedure does not interfere with the normal extraction process. In a patented process<sup>194</sup> for the preparation of stabilised alumina, aqueous sodium aluminate is neutralised to a  $p_H$  value of less than 9.8 with sulphuric acid to precipitate a gel containing basic aluminium sulphate; an alkali silicate is then added to a suspension of the gel so that the SO<sub>4</sub>'' is replaced by SiO<sub>3</sub>''. Finally the product is washed and calcined. In another method<sup>195</sup> for producing an alumina gel, an alumina sol is suspended in a viscous inert liquid such as a petroleum oil containing an organic base, *e.g.*, morpholine.

The use of lead-lined tanks for the preparation of alum solutions has not been satisfactory and E. S. Hopkins<sup>196</sup> suggests replacement of the lead by an impervious thermoplastic membrane made of synthetic resin, magnesium silicate and a chlorinated hydrocarbon, and faced with acid-proof bricks. According to E. A. Gee, W. K. Cunningham and R. A. Heindl<sup>197</sup> iron-free alum can be produced in a continuous process by treating an aqueous solution of crude alum with alcohol under conditions in which the ferrous and ferric sulphates are soluble while the alum is insoluble. Such a process however, although technically possible, was economically unsound, although the possibility of using expensive organic solvents for the preparation of cheap inorganic compounds was demonstrated.

### *Silicon, titanium and zirconium*

Silicon ingots can be prepared by melting silicon in a thin-walled silica crucible which is then heated for an hour at 1450–1550° c. When the crucible is withdrawn from the furnace the silicon breaks away from

the walls and interior strains in the ingot are avoided.<sup>198</sup> J. T. Kendall and D. Yeo<sup>199</sup> have described the preparation of pure silicon carbide by passing the vapours of an organic silicon compound over a heated carbon filament. Amorphous finely-divided silica is suitable as a base for pigments, catalysts or insecticides and according to a patented method<sup>200</sup> it can be made by mixing siliceous material with a material such as carbon and heating to 1250–1450° C. The gaseous silica evolved is removed from the reaction zone and, while still at the reaction temperature, it is treated with an excess of air to form finely divided  $\text{SiO}_2$ . The physics and chemistry of the fusion of  $\text{SiO}_2$  and commercial methods of producing fused silica have been discussed by B. A. Rogers, W. J. Kroll and H. P. Holmes.<sup>201</sup> Under the best operating conditions, the power consumption was about 63 kw. hr. per 40 lb. ingot of  $\text{SiO}_2$ . It is believed that the consumption could be reduced to about 1 kw. hr. per lb. of fused silica. Silica gel finds some use for addition to cement mixtures and a product suitable for this can be made by adding 5–10% of a mineral acid to aqueous sodium silicate to precipitate a hydrated silica. The gel particles are suspended in an aqueous medium to which a surface-active agent or emulsifying agent has been added.<sup>202</sup> Another new process<sup>203</sup> for the manufacture of silica gels describes how the reactant solutions are impinged at a high velocity on a rapidly rotating horizontal plate. The sludge produced is thrown off by centrifugal force, then collected and washed. According to K. G. Mathur,<sup>204</sup> the activity of some precipitated silicates is as high as that of activated carbon. The methods of preparation of the silicates of iron, alumina, manganese, chromium, magnesium, calcium, nickel and copper are described together with their bleaching tests on vegetable oils.

In a patented process<sup>205</sup> for the manufacture of titanium hydride, titanium dioxide and calcium hydride are allowed to react at an elevated temperature in a reducing atmosphere. The reaction zone is then evacuated to remove the hydrogen and to distil off the excess calcium. Hydrogen is then passed into the heated reaction zone to convert the titanium into the hydride. A pilot plant method for the purification and distillation of titanium tetrachloride is described by C. K. Stoddard and E. Pietz.<sup>206</sup> Vanadium is first removed by adding copper powder at 100° C.; then, after settling, silicon tetrachloride is removed by blowing the liquid into a steel boiler fitted with a fractionating column. In the hydrolysis of titanium solutions it is necessary to use a seed as a nucleating agent and a patented process<sup>207</sup> proposes to use a dispersion of orthotitanic acid containing 20–90 gms. of  $\text{TiO}_2$  per litre. This is made by dispersing the titanium dioxide in hydrochloric acid or nitric acid in the presence of 0.5–6.5% (on the  $\text{TiO}_2$  content) of sulphuric acid which acts as a stabilising agent. Seeds which are similarly used for the production of rutile titanium dioxide are, according to a patented process,<sup>208</sup> made by heating  $\text{TiOSO}_4$  in aqueous solution to precipitate  $\text{H}_4\text{TiO}_4 \cdot \text{SO}_3$ , which is treated with hot sodium hydroxide to remove excess acid. This makes an alkali titanate which is washed with water and treated with hydrochloric acid to form the rutile seeding agent. In another patented process<sup>209</sup> for the manufacture of rutile, a washed pulp of hydrated titanium dioxide, obtained by hydrolysis, is diluted with water and mixed

with basic titanium chloride seed slurry. After the mixture is filtered and washed until free from titanium chloride, the cake is mixed with solutions of ferrous ammonium sulphate and potassium carbonate, dried and calcined at a temperature rising from 300 to 975° c. over a period of 5 hours. The temperature is then held at 1000° c. for 4 hours.

In a patented process<sup>210</sup> for the manufacture of zirconium hydride, a zirconium compound is treated with an alkaline earth metal at an elevated temperature and the zirconium thus formed is reacted with hydrogen. Zirconium oxide can be produced by heating zircon with carbon in an electric furnace and then burning the compounds formed to zirconium oxide by igniting a thin layer of the compound on a lightweight fire-brick hearth.<sup>211</sup> The production of zirconium oxide in Germany has also been described.<sup>212</sup> The Brazilian ore was treated with concentrated sulphuric acid at 180° c., the product leached with water and the solution evaporated to deposit a precipitate which was washed and calcined to give the zirconium oxide. It has been proposed to purify anhydrous zirconium chloride by distilling it from a mixture containing a sulphide of zirconium, zinc, magnesium, calcium, or sodium. This treatment removes traces of iron, alumina and silicon.

### *Hydrogen peroxide*

J. Sertl<sup>214</sup> has reviewed the chemistry, preparation, properties, detection, determination and uses of hydrogen peroxide. Hydrogen peroxide of 90% strength is made by distilling hydrogen peroxide at a  $p_H$  of 3-5 at a reduced pressure in a climbing-film evaporator.<sup>215</sup> The vapour passes into a separator where the hydrogen peroxide vapour is withdrawn as the overhead product and liquid hydrogen peroxide and impurities form the bottom product. The vapour passes to a fractionating column where concentrated hydrogen peroxide is removed as the bottom product and water vapour as the overhead product. A second similar distillation is required to produce 98% hydrogen peroxide. E. S. Shanley and F. P. Greenspan<sup>216</sup> have summarised the physical properties of 90% hydrogen peroxide. They also describe briefly the reactions of 90% hydrogen peroxide with various groups of organic substances and its fire and explosion hazards. Containers for high strength hydrogen peroxide are best made of 99.6% aluminium which has been subjected to a pickling treatment with sodium hydroxide followed by sulphuric acid (10%). Suitable materials for handling this high strength product are also mentioned. The production of high strength hydrogen peroxide for rocket propulsion has been described by V. W. Slater and W. S. Wood.<sup>217</sup> Data is also given on the physical properties and stability of high strength hydrogen peroxide, and the corrosion and handling problems involved with this product are discussed. The application of high strength hydrogen peroxide to propellant systems is surveyed by W. H. Wheeler, H. Whittaker and H. H. M. Pike.<sup>218</sup> The method of manufacturing 80-85%  $H_2O_2$  is outlined. Approximate thermodynamic methods of calculating the composition and temperature of the gaseous products from this fuel are given and the mechanical performance is also calculated.

*Dielectrics*

Titanium dioxide is well known as a dielectric material and, according to a patented process,<sup>219</sup> it can be rendered water-repellant by exposing it to the vapours of an organic silicon halide. It is then mixed with 10–60% of a synthetic resin or rubber for use as a dielectric material. Another titanium dielectric composition<sup>220</sup> consists of a mixture of titanates, zirconates and stannates of the alkaline-earth metals which has been fired at 1340–1370° for 3 hours. Another electrical insulating composition<sup>221</sup> having a high dielectric constant is manufactured by firing a mixture of titanium dioxide and titanate at 590–760° c. with mica and a finely-divided glass frit. A further dielectric material<sup>222</sup> is made by loading a binder, *e.g.*, lead borate glass, with a mixture of previously fired and powdered barium and strontium titanate mixtures. Another patented process<sup>223</sup> for making an electrical insulating composition modifies the relative proportions of cryolite, boric acid, alkali and lead, commonly used in making glass, to make an insulating material. If the ingredients are worked up in two stages greatly improved insulating properties are obtained.

*Luminescents*

Recent developments in infra-red sensitive luminescents have been reviewed by G. F. J. Garlick.<sup>224</sup> Numerous patents have been taken out for the manufacture of luminescents in general.

A method patented by Marconi Wireless and Telegraph Co.<sup>225</sup> consists of heating the constituents under pressure and crystallising the phosphor from the vapour phase. In another patented process,<sup>226</sup> the luminescent is suspended in a fluid and the finer particles are attracted by, and deposited on, an electrically charged support. The layer is bound by spraying with a mist of phosphoric acid. Another patent<sup>227</sup> describes the manufacture of a phosphor for use in low-pressure mercury-vapour-discharge lamps. Calcium phosphate is first prepared by heating calcium carbonate with ammonium phosphate. The calcium phosphate is then mixed with a compound of chlorine and/or fluorine, *e.g.*,  $\text{CaF}_2$  or  $\text{SrCl}_2$ , and an activator (a manganese or antimony compound) which has been fired in an atmosphere of chlorine at a temperature lower than the melting point of the mixture.

The use of titanium-activated calcium silicate is recommended in a patented process by the General Electric Co.<sup>228</sup> Calcium carbonate and silicic acid are mixed to a paste with an aqueous solution of titanous sulphate. The paste is dried and calcined at 1000–1200° c. A manganese compound may be added as an additional activator.

J. Brennan<sup>229</sup> employs another range of compounds for the manufacture of luminescents. The tungstates of thallium, cerium and magnesium are prepared by firing a mixture of magnesium and sodium chlorides and sodium tungstate, with thallium chloride or cerium oxide. The sodium chloride is removed with water and the residue is re-fired at 1100° c. Another method using magnesium tungstate, made from magnesium oxide and ammonium tungstate, is described in a patent taken out by British Thomson Houston.<sup>230</sup>

Another patent<sup>231</sup> describes a method for producing a phosphor which will give a red fluorescence in mercury-vapour lamps. A mixture of zinc and beryllium oxides, together with manganese carbonate and silicic acid, is fired at 1220–1260° c. The maintenance of fluorescence brightness is improved by a slight excess of beryllium or magnesium oxide. A wide range of colours can be imparted to the phosphors for general illumination purposes by replacing the calcium with barium or strontium, and the fluorine by chlorine or bromine. A. H. McKeag and P. W. Ranby<sup>232</sup> describe the preparation and characteristics of manganese-activated zinc and beryllium silicates and of the alkaline-earth halogen-phosphate phosphors of the fluorapatite type. The production of  $3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$  is particularly described. The preparation of a yellow fluorescing manganese-activated zinc silicate is described in another patent.<sup>233</sup> The zinc oxide and silica mixture, together with a small amount of manganese oxide or silicate, is fired at 800–850° c. in a non-reactive or reducing gas, *e.g.*, nitrogen, hydrogen or carbon monoxide, in the presence of a non-persistent catalyst such as steam or boron trioxide.

Uranium salts are also used in the production of luminescent compounds.<sup>234</sup> Chloro-, fluoro- or chloro-fluoro-phosphates of barium are activated by 6–7% of uranium oxide. Barium phosphate and barium chloride and/or fluoride are heated at 900–1000° c. with the required amount of uranium oxide, or a uranium salt which gives the oxide on heating.

White fluorescing phosphors can be produced by mixing manganese-activated zinc-beryllium silicate with silver-activated zinc sulphide.<sup>235</sup> The manganese-activated zinc-beryllium silicate is prepared by heating a mixture of zinc and beryllium oxide with silica for 2–6 hours at 1280° c. and the silver-activated zinc sulphide is heated for 25 minutes at 900° c. Zinc sulphide or zinc sulphide-cadmium sulphide phosphors can be improved according to a patent<sup>236</sup> by firing in the presence of a flux containing an alkali, alkaline-earth and hydrogen-containing halide. An example is a mixture of zinc and cadmium sulphides with sodium, barium and ammonium chlorides. The mixture is moistened with an aqueous solution of copper sulphate, dried, fired at 1250° c., cooled and washed.

Some difficulty has been experienced in grinding phosphorescent materials, such as zinc sulphide, without impairing their phosphorescent properties. A suitable method is described by Eastman Kodak.<sup>237</sup> The coarse zinc sulphide is ground in an organic solvent containing a fatty acid, *e.g.*, stearic acid. The liquid is decanted and the residue heated at about 70° c., *i.e.*, at approximately the melting point of the fatty acid, until the solvent is completely evaporated. The stearic acid-coated powder is mixed with plasticised cellulose nitrate in the solvent for application to phosphorescent screens.

F. A. Kröger<sup>238</sup> describes and discusses the suitability of luminescent substances for cathode-ray tubes used in oscillographs, television receivers, etc., and for the detection of infra-red rays. A cathode-ray tube screen, built up of three phosphors, is described in a patent.<sup>239</sup> The first (silver activated-zinc sulphide) is excited by the beam of the tube. The second

(copper-activated zinc or zinc-cadmium sulphides) is activated by the light emitted by the first, and the third (manganese-activated magnesium fluoride with or without zinc or beryllium) emits a colour different from the second and has no build-up effect and a shorter time lag, so that the screen emits a light of one colour when a spot is excited a certain number of times, and of a different colour when it is excited a smaller number of times.

A. H. McKeag and P. W. Ranby<sup>240</sup> describe the use of phosphors in the production of a lamp which gives substantially natural colour-rendering of the objects illuminated.

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## FUEL

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THE year has seen the nationalisation of the gas industry in Great Britain placed on the Statute Book in addition to those of the coal and electricity industries and the introduction of a Bill to effect the same process for the iron and steel industry, which is one of the biggest industrial consumers of fuel. In a paper<sup>1</sup> by M. G. Dessus and M. P. Fleurquin the principles adopted by the nationalised gas and electricity industries of France in fixing tariffs are discussed.

The Parliamentary and Scientific Committee<sup>2</sup> has submitted to Sir Stafford Cripps and to the Minister of Fuel and Power a further Report advocating priority for the manufacture of modern combustion appliances estimated to be capable of saving 18 million tons of coal per annum. W. Moncrieff-Carr<sup>3</sup> has put forward a ten-year plan calling for a four-fold expansion of the carbonising industry.

The Fuel Efficiency Committee<sup>4</sup> of the Ministry of Fuel and Power has been reconstituted with fresh terms of reference. In addition to the Central Committee in London, there are now also Regional Committees. In the first Annual Report of the Advisory Council on Scientific Policy,<sup>5</sup> the Ministry of Fuel and Power was recommended to appoint a Chief Scientific Officer and a Scientific Advisory Council. This has been followed by the appointment<sup>6</sup> of Dr. H. Roxbee Cox as Chief Scientist and of a Scientific Advisory Council under the chairmanship of Sir Alfred Egerton. A sub-station of the Fuel Research Station<sup>7</sup> to be mainly concerned with domestic appliances is being set up in Scotland as part of a group of additional research facilities. The scientific activities of the National Coal Board have been described.<sup>8</sup> In addition to scientific "day-to-day" control, research will be carried out at national level.

A notable publication<sup>9</sup> during the year has been a companion book to the *Efficient Use of Fuel*. The new book, entitled the *Efficient Use of Steam*, by O. Lyle is published under the auspices of the Fuel Efficiency Committee of the Ministry of Fuel and Power. The Proceedings of the "Fuel and the Future" Conference organised by the same Ministry have also been published,<sup>10</sup> and the material in the *Statistical Digest* extended<sup>11</sup> till the end of 1947.

### Fuel resources and production

In searching for oil, indications have been obtained<sup>12</sup> of the possible existence of coalfields in a number of unsuspected areas of Great Britain. Coal has been proved in Central Lincoln and may exist (1) in Shropshire and between there and Burton-on-Trent, (2) in Wiltshire as an extension of the Somerset field, (3) in the Cotswold district of Gloucester and in South Worcestershire, (4) in Oxfordshire, and (5) in East Essex. The reserves of coal below the Cheshire Plain have been considered by G. H. Greenwell,<sup>13</sup> The reserves, production and qualities of the N. Staffs,<sup>14</sup>

the Yorkshire coalfield,<sup>15</sup> and the Derby, Notts. and Lincoln<sup>16</sup> coalfields have been surveyed. J. G. King<sup>17</sup> examines the reserves and production of the types of coal in Great Britain suitable for gas manufacture and concludes that ample supplies can be foreseen.

It is estimated<sup>18</sup> that 1½ million tons of lignite have been located at Bovey Tracey and that monthly production will soon reach 15,000 tons. Some 1,300 tons of coal and anthracite were raised from the Antrim field of N. Ireland in 1947.<sup>19</sup> Borings in Tyrone County have also revealed the existence of coal.

H. S. Elford and M. R. McKeown<sup>20</sup> have published a detailed account of the Australian black and brown coal industries. To meet demands, new fields of brown coal are being opened up in Victoria.<sup>21</sup> Production<sup>22</sup> of Leigh Creek sub-bituminous coal north of Adelaide is increasing and it is hoped shortly to reach 8,000 tons weekly.

The Princeton sub-bituminous coalfield of British Columbia is considered<sup>23</sup> to contain 300 million tons and to be capable of yielding 300,000 tons p.a. The coal reserves of India are estimated<sup>24</sup> at 16,500 million tons, but coking coals may not exceed 700–750 million tons. A sound policy of conservation is said to be required. New Zealand coal production amounted<sup>25</sup> in 1946 to 2,800,000 tons. Two coalfields each of about 30 million tons have been discovered<sup>26</sup> north of Bulawayo in Southern Rhodesia.

A deposit of high grade anthracite together with bituminous coal has been found<sup>27</sup> near Middelburg, S. Africa.

In Poland, 1947 production<sup>28</sup> reached 59 million tons of hard coal, of which 17 million tons were for export. An additional 3–4 million tons of brown coal are also mined. The coals of S. Sakhalin have been surveyed.<sup>29</sup> They range from brown coal to anthracite. A. B. Crichton has criticised<sup>30</sup> the estimates of the U.S. Bureau of Mines for the U.S.A. coal reserves as erroneous and misleading and submits much smaller figures which give a life of only 250 years. In the U.S.S.R. coal output is to reach<sup>31</sup> 250 million tons by 1950.

The Geological Museum has published<sup>32</sup> a number of detailed studies of the carboniferous rocks in various areas of Great Britain. L. R. Moore has described<sup>33</sup> the East Crop in S. Wales between Pontypool and Risca.

R. A. Mott has surveyed<sup>34</sup> the existing methods of classifying coals, of which those of the A.S.T.M. and Seyler are considered the more exact. The various types and ranks of coal are then discussed country by country throughout the world. It is pointed out that the rank of coals (exclusive of durains and fusains) is an indication of many important properties, particularly of swelling power on which the uses of coals depend. Mott proceeds to describe his proposed classification of coals based on plotting on a graph the volatile matter and calorific value of dry mineral matter free coal (Parr basis). Lines for carbon and hydrogen may then be superimposed. With the chart a rough estimate can be made of the properties of a given coal such as the agglomerating or swelling power, the coking power in coke ovens, thermal yields of gas on carbonisation, etc. The classification is considered to be world wide in application and to be of value to workers carrying out research on coals from widely different coalfields.

### *Peat*

Information on the properties, winning, harvesting, and utilisation of peat has been summarised.<sup>35</sup> It is concluded that 1000 million tons of air-dried peat could be won in Great Britain but the cost is unlikely to be less than that of coal except in inaccessible districts. G. K. Fraser<sup>36</sup> has described the principal types of plants which contribute to peat formation. The Scottish Reconstruction Committee is considering<sup>37</sup> the development of mechanised peat winning with associated by-products industries. A new sphagnum peat plant has been established<sup>38</sup> in Scotland. A model for pumping peat of 91% water content has been described.<sup>39</sup> A method of de-watering peat down to 37% moisture by heat and pressure is reported.<sup>40</sup> Studies of the extraction of wax<sup>41</sup> from peat and of the thermal decomposition<sup>42</sup> of peat have been made in Sweden. All peat samples on heating showed endothermic effects below 225–300° c. Exothermic and endothermic effects were obtained at higher temperatures depending on the extent of decomposition of the peat.

### **Physical and chemical properties of coal**

#### *Flora and fauna of coal*

A sequence of ten marker bands in the Notts and Derby area has been established.<sup>43</sup> Correlation with Yorkshire and neighbouring coalfields is indicated. Correlation of seams<sup>44</sup> in the middle Ruhr district has become possible by means of a lingula band. Examination<sup>45</sup> of Scottish limestone coals has revealed at least 90 types of spores, many of them new.

#### *Physical properties of coal*

C. A. Seyler has described<sup>46</sup> his work on the reflectivity of coal which has resulted in the identification of a succession of components in coal, nine in all. Mineralogical and petrographic methods have been used<sup>47</sup> by M. T. Mackowsky in the development of coal preparation processes. B. G. Simek<sup>48</sup> has attempted the calculation of the mechanical strength of coal, coke and briquettes based on the tumbler and similar tests. A micro ball mill has also been used<sup>49</sup> for the same purpose. The plastometric method has been applied<sup>50</sup> to the investigation of 35 Polish coals. The plastic deformation of small particles of coal under compressive forces has been examined.<sup>51</sup> It appears that shearing takes place at the intermicellar boundaries between which only relatively weak physical forces are acting.

Finely ground boghead or sapropelite coal is stated<sup>52</sup> to be suitable as a filler in many rubber products in plastic leather substitutes, etc., but possesses low activity and in consequence it cannot be used completely as a substitute.

#### *Chemical properties of coal*

The variations in rank have been examined of the petrographic constituents of banded Illinois coal<sup>53</sup> and of the meta-anthracite<sup>54</sup> of Rhode Island, U.S.A.

H. L. Riley has reviewed<sup>55</sup> a number of aspects of the molecular structure of coal. W. R. Ruston has calculated<sup>56</sup> the C–C spacing in

various coal samples and finds that low-rank coals show hydroaromatic nature. On carbonisation the C-C spacing changes to the value for aromatic structures. F. M. Trotter<sup>57</sup> has made a detailed study of the changes in volatile matter in both horizontal and vertical directions in the S. Wales coalfield and correlates these trends with the distance from an inclined plane of shearing stress which rises towards the north-west and breaks surface beyond the limits of the coalfield.

*Inorganic constituents.*—Spectrographic analysis of the ash has been used<sup>58</sup> to differentiate Asturian coals. The elements which are useful for this purpose are discussed. The V and Cr contents of 27 Japanese coals are reported.<sup>59</sup> The ratio of  $V_2O_5 : Cr_2O_3$  is usually greater than unity.

*Oxides of nitrogen in carbonisation gases.*—Both F. Magot-Cuvru<sup>60</sup> and F. Plotegher<sup>61</sup> have reached the same conclusion, that oxides of nitrogen are only formed during carbonisation when air is permitted to be present.

*Pyrolysis.*—A. Gillet has continued<sup>62</sup> his work of testing the hypothesis that carbonisation is an acceleration of the natural processes proceeding during geological ages at temperatures below 100° C. K. S. Zarembo distinguishes<sup>63</sup> between reactions inside the lumps of coal during pyrolysis from those between the lumps. The latter are designated "secondary reactions." The investigation of these reactions is described and reaction mechanisms discussed.

*Sulphur.*—T. Fraser and W. L. Crentz<sup>64</sup> show that the organic sulphur is roughly the same in all the gravity fractions of four American coals but the pyritic sulphur increases with increase in specific gravity of the fraction as might be expected. The sulphur in Assam coal<sup>65</sup> is found to be almost wholly organic. During carbonisation at least 66% of the sulphur is removed. Carbonisation in presence of lime removes 77% and, in presence of calcium chloride, 89%. Fixation of sulphur in the coke is shown to be due to interaction of the coal and volatile sulphur compounds. D. T. Davies has reviewed<sup>66</sup> the techniques for recovering pyrites from colliery refuse for use in sulphuric acid manufacture. Recovery has only a slight effect on the sulphur content of the coal.

*Oxidation of coal.*—H. C. Howard has discussed<sup>67</sup> the reactions of coal with oxygen at temperatures below those of active combustion. A. Romwalter thinks<sup>68</sup> self-ignition of Hungarian coal is promoted by alkaline water. The heat of wetting, using both methyl alcohol and water is suggested<sup>69</sup> as a simple means of assessing the quality of newly-found coal seams. Eight coals ranging from lignite to anthracite have been oxidised<sup>70</sup> by oxygen in the presence of 5% NaOH. Their behaviour was compared with that of the same coals after dimethyl sulphate treatment. Methylation was found to reduce but not remove susceptibility to oxidation. It was more effective with high volatile bituminous coals than with low volatile and anthracitic coals. The electrolytic oxidation of coal has also been investigated<sup>71</sup> with a view to the production of carbon chemicals. The distribution of nitrogen<sup>72</sup> in the products of alkaline permanganate oxidation of coals of different rank suggests that condensed structures containing the same kind of nitrogen linkages are common to all. Yields are reported of mellitic acid<sup>73</sup> as high as

29% of the coal by oxidation with nitric acid followed by alkaline permanganate.

*Humic acids.*—T. S. Polansky and C. R. Kinney have found<sup>74</sup> that organic solvents can extract 80–85% of the humic acid-like material in bituminous coal after it has been treated with nitric acid. The structure of acid-precipitated humic acids<sup>75</sup> is destroyed by freezing to  $-3^{\circ}\text{C}$ . and after thawing, filtration is facilitated.

*Hydrogenation studies.*—The work of Neuworth has been continued by A. N. Basu and R. A. Glenn<sup>76</sup> on the chromatographic separation of the primary products of coal hydrogenation. A fraction containing a quarter of the total oxygen of the coal in a form other than hydroxylic has been obtained. Glenn has also continued studies<sup>77</sup> of the step-wise hydrogenation of coals from Pocahontas No. 3, High Splint and Illinois No. 6 seams. The properties of the oils obtained were found to be similar irrespective of the rank of the coal from which they were derived. Other studies<sup>78</sup> of the various stages of coal hydrogenation have shown that tin catalysts are the best for the primary cracking of the coal. A Zn-Sb alloy was however the most satisfactory catalyst for decreasing asphaltenes in the product. A three-component catalyst consisting of 0.5% of Sn and 0.5 Zn-Sb alloy gave good results which were little improved by increasing the percentage to 2%. More asphaltenes are obtained in the presence of, than in the absence of, vehicle.

*Solvent extraction.*—The recovery of Montan Wax<sup>79</sup> from coal found at Karlovy Vary, Czechoslovakia, has been described. Consideration is also being given<sup>80</sup> to the commercial possibilities of the 10–13% of wax to be found in certain lignites of Arkansas and California. Utah bituminous coal<sup>81</sup> also contains a fossil resin which can be used as a substitute for lac-resin in the preparation of dielectric varnishes.

### Coal mining and preparation

The rapid development of drift mining is expected<sup>82</sup> to add 3–4 million tons p.a. to the output in Great Britain. The Chief Inspector of Mines has discussed<sup>83</sup> many aspects of modern mining methods and indicated lines of progress to be welcomed. British and American mining methods have been compared.<sup>84</sup> Only 25% of those employed at mines in Great Britain work at the face, the comparable figure in the U.S.A. is 70%. Safety aspects and the training of personnel at mines in Holland and Germany have been investigated.<sup>85</sup>

More detailed information is now available<sup>86</sup> of the experiment in underground gasification at Gorgas, U.S.A. With an air blast, the average C.V. of the gas produced was 47 B.Th.U./cu. ft. The efficiency of gas production was 41%. Preparations are also being made<sup>87</sup> by a Belgian syndicate for an experiment near Liège. The same syndicate has conducted<sup>88</sup> an experiment on an Italian lignite which contained 55% water and 25% ash.

*Coal dust problems.*—H. A. J. Pieters and J. N. J. Hovers have used<sup>89</sup> a modified Godbert and Wheeler apparatus to study explosions in dust clouds. They conclude (1) that the mineral constituents of the coal are more effective in making a dust cloud non-explosive than the mixed inert dust, (2) mixtures of dust from different coals are relatively more

explosive than was to be expected from the volatile matter of the mixture, and (3) clouds of particles 75–120  $\mu$  can be explosive although the Godbert and Wheeler apparatus gives no such indication.

*Handling and storage of coal.*—W. H. Dunkley<sup>90</sup> has described the successful stocking of coal by bulldozer to a depth of 20 ft., which is much in excess of the recommended depth.

The particle size distribution resulting from some breakage processes has been re-studied.<sup>91</sup> The National Coal Board has decided<sup>92</sup> to accept the Report on Coal Grading and Sizing referred to in last year's Report (Ref. No. 97).

*Coal drying.*—W. J. Kramers and J. H. McKee have reviewed<sup>93</sup> comprehensively the forms in which water may be present in coal and the nomenclatures adopted for the varieties, together with the many diverse processes for de-watering and drying coal. A cyclone de-waterer developed in Holland has been found<sup>94</sup> to thicken coal slurries to 60–65% solids, but the fines less than 200-mesh are largely lost in the effluent.

*Coal cleaning.*—F. W. Mayer<sup>95</sup> has considered the theory of coal-washing processes and the ways in which the suspended particles behave. To test the efficiency of a cleaning process he recommends the use of an artificial test material such as a setting plastic filled with  $\text{BaSO}_4$  rather than coal. G. S. Haslam also examines<sup>96</sup> the assessment of washing performance based on a method suggested by Tromp involving the construction and application of "error curves." The washability characteristics of over 140 Indian coals have been examined.<sup>97</sup> A useful bibliography of information on the formation, recovery, up-grading, and utilisation of coal slurries has been prepared.<sup>98</sup>

The development of electrostatic coal cleaning is taking place<sup>99</sup> in the U.S.A. Coal less than  $\frac{3}{8}$  in. size and moisture of about 1.5% is required. Details and operating results of the Denby Hall centralised coal preparation plant have been given.<sup>100</sup> The plant includes Barvoys dense medium separation, Hoyois trough washing and froth flotation for fines.

*Briquetting.*—The briquetting industry in the U.S.A. has reached a record output of 3 million short tons in 1946.<sup>101</sup> The proportion of anthracite briquetted is rising; 6–7% of asphalt is the normal binder. Canadian work on briquetting of various coals with different binders is reported.<sup>102</sup> With Drumheller non-caking coal, 20% of good caking coal was required to give a briquette which had a good performance in a fire. Good briquettes have been successfully obtained<sup>103</sup> from Leigh Creek, S. Australian coal in the absence of binder by proper attention to sizing and moisture content.

### Coke properties

*Quality.*—The effect on the oxidation of coal of storage has been studied<sup>104</sup> for 11 American coals. It was found that the resulting coke strength had decreased by some 15% after 5 years. The A.S.T.M. tumbler stability test has been used<sup>105</sup> to study the strength of coke made from pulverised coals. Coal quality was confirmed as the most important variable affecting coke strength. Pre-heating of the coal to 244° c. had no effect on coke strength although coking time was reduced. P. E. Jordan has stressed<sup>106</sup> the need to produce coal low in ash and sulphur

and of great uniformity for coke-making. Pulverising of the coal improves the stability and hardness of coke without the use of excess of low volatile coal. Stability and hardness of the coke above a minimum value is regarded as of decreasing value for blast furnace work. The replacement is suggested<sup>107</sup> of the time-consuming screen analysis of coke for blast furnace use by a determination of the aerodynamic properties of bulk coke. The latter requires only 30 seconds. The properties required in coke for foundry work have been reviewed.<sup>108</sup>

N. R. Kouchairevitch finds<sup>109</sup> that the pressure developed during carbonisation varies between 0.03 and 0.3 kg./cm.<sup>2</sup> according to the type of coal. W. A. Selvig and W. H. Ode<sup>110</sup> have added to B.S. Spec. 1016 for the test for the swelling index of coal, provision for assessing coke-buttons which do not conform to standard profiles.

A very important study<sup>111</sup> has been made by the British Coke Research Association of the pressures developed on the walls of a coke-oven during carbonisation. For this purpose a special test oven with one movable wall was employed on which the pressure was measured. The experiments were carried out with a range of British coals, of widely different volatile matter from 13.2 to 39.4%. It was found that in general between 14 and 30% volatile matter, the swelling pressure increased with decreasing volatile matter. Above 25–30% coals exerted little, or no pressure. The maximum pressure was progressively found to decrease with decreasing bulk density. Reduction in the rate of carbonisation and increase in the width of the oven had little effect. It is considered that these tests give a better indication of the liability of a coal to develop pressure during coking than the various laboratory tests, such as Kopper's, Nedelmann's and Gieseler's.

Simek and others investigated<sup>112</sup> the reactivity of coke by reaction with oxygen using a modified Kreulen apparatus. They confirm that reactivity is increased by using lower coking temperatures and shorter coking time and decreased by using coal blends of higher bulk density. Mineral inorganic additions such as  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  were found variable in effect. For evaluating coke for water gas and producer gas manufacture, M. Delassus and R. Devaux use<sup>113</sup> a mixture of steam and nitrogen at 1000° C.

*Low-temperature coke.*—Details are now available<sup>114</sup> of the preparation of low-temperature coke from non-coking coals by first briquetting with residues from the commercial hydrogenation of coal. These residues have high coking power and impart this to the non-coking coal. A large plant is under erection<sup>115</sup> by the Disco Company in the U.S.A. to produce a smokeless fuel from coal fines which are first preheated to modify their coking properties before being carbonised in inclined rotating kilns at 455° C. A pilot plant using non-coking coal has been operated<sup>116</sup> at West Frankfort, Illinois, and produces from 10–48 mesh fines a domestic smokeless fuel larger than 2 in.

## Combustion

A. Gosselin points out<sup>117</sup> that the three maxima at 200A, 2350A, and 2800A in the spectrum of the combustion of carbon have energies corresponding with the calculated values for the heats of formation of  $\text{CO}$  and  $\text{CO}_2$  from atomic carbon and atomic or molecular oxygen. R. F.

Strickland-Constable considers<sup>118</sup> that above 1000° c. the primary product of the reaction of carbon and oxygen is CO and not CO<sub>2</sub>. R. Audibert, however, finds<sup>119</sup> that above 1500° c. and at low pressures the reaction is:  $3C + 2O_2 \rightarrow 2CO + CO_2$  and thinks a chain reaction is indicated. A. A. Orning has described<sup>120</sup> an apparatus for determining the reactivity of solid fuels to oxygen using adiabatic self-heating. The order of the reaction with oxygen is found to decrease from about one with cokes and anthracite to nearly zero for lignites. Gumz has reviewed<sup>121</sup> the chemical, physical, and thermodynamic bases of combustion and considered some practical applications. The reactions between carbon, oxygen, and steam have also been studied<sup>122</sup> on behalf of the American Gas Association and equilibrium concentrations calculated over wide ranges of temperature, pressure and oxygen to steam ratios. The equilibria between steam and carbon dioxide with carbon have been examined by W. K. Lewis,<sup>123</sup> who points out that the difficulties inherent in the water-gas and producer-gas processes of obtaining the heat of combustion where it is most wanted, are solved by adopting the fluidised bed technique.

The burning of individual particles of coal of the size used in pulverised fuel firing has been studied<sup>124</sup> by A. A. Orning. The assumption that the coke residue burns subsequently to the evolution and combustion of the volatile matter was confirmed.

A detailed study of the use of oxygen and oxygen-enriched air in high-temperature heating processes has been undertaken by H. R. Fehling.<sup>125</sup> Tables are given of combustion data for the various solid, liquid and gaseous fuels with varying degrees of enrichment. Consideration is given to the composition of the combustion products at temperatures of 2000–3000° c. where dissociation is extensive, when using oxygen. In practice, it is pointed out that the thermal efficiency of a furnace using oxygen depends very much on the fuel and that the energy required to produce the oxygen must also be taken into account. The conditions where the waste heat available and the power for oxygen production balance are examined from which it is clear that low C.V. gases containing much nitrogen such as producer-gas and blast furnace gas are not attractive fuels for oxygen enrichment. For higher grade fuels, 70% over-all thermal-efficiency is attainable with oxygen enrichment of 70–100%. The effect of the high temperature resulting is likely to be injurious to brickwork unless means can be found of controlling the direction of heating.

### Fuel utilisation

*Industrial boilers.*—According to V. Walker<sup>126</sup> there has been no radical change in American boiler practice recently, only detailed developments regarding reduced mass flow velocity, arrangement of air heaters, etc. F. W. Lawton reviews<sup>127</sup> the trend in British practice towards units of more than 200,000 lb./hr., steaming capacity. The spreader stoker is believed to avoid high temperature bonded deposits and thus increase boiler availability. W. S. Patterson describes<sup>128</sup> the factors to be taken into account when selecting steam generating units. Water-tube boiler plant of special application to the iron and steel industry is described by<sup>129</sup>

Davis and others. It is concluded that future progress depends on advance in the production of suitable alloy steels and the development of satisfactory processes of fabrication. A. Meyer also considers<sup>130</sup> the possibilities of using higher temperatures. Developments in steam turbines over recent years have been reviewed.<sup>131</sup> W. R. Felix considers<sup>132</sup> the growing competition between steam turbines and gas turbines and concludes that the steam turbine will remain important in large power plants on account of high over-all efficiency. He emphasises the profound influence which the initial steam conditions have on over-all thermal efficiency and enters into the costing of steam plant. As a result of their experience with the cyclone burner, the Commonwealth Edison Co. of Chicago are adopting<sup>133</sup> the burner as standard for all additions to its generating plant.

Brown coal firing in Victoria is providing<sup>134</sup> problems associated with designing a stoker suitable for widely varying capacity. Conventional chain-grates require the use in addition of bituminous coal or fuel oil. The Phoenix controlled feed underfeed stoker has been described.<sup>135</sup> The design obviates packing of the feed and undue wear of the feed screw even on coal slacks, coke, and coke breeze.

A. C. Dunningham<sup>136</sup> has examined the flue gas losses with coal and oil firing respectively and then made a direct comparison of coal and oil firing on a water-tube boiler and a Lancashire boiler. Slightly greater outputs and efficiencies were obtained on oil but since the price of oil on a thermal basis was about 1.8 times that of coal, oil firing was about 50% more costly than coal.

E. B. Neil has examined<sup>137</sup> the design of steam plants for road vehicles in the light of recent developments and concluded that acceptable thermal and over-all efficiencies could be attained by incorporating the high rates of heat release, etc., which are now available. Steam cars of the past are also surveyed.

The use of secondary-air in boilers has been surveyed by N. Y. Kirov.<sup>138</sup> The use of over-fire jets of both air and steam is old-established, but during the war, economy and the need to reduce smoke from marine boilers led to renewed attention being paid to such devices which has continued into peace time. One of the most interesting of these is the Courtauld steam-jet system,<sup>139</sup> in which a row of small steam jets is arranged across the mechanical stoker just beneath the guillotine and is arranged to draw combustion gases and air back over the unignited coal and assist ignition. The device has been found particularly useful with high ash coals (up to 43%) and enables boiler output to be maintained on fuels with which, otherwise, it would be impossible.

*Boilers cum gas-turbines.*—Two further forms of pressure boilers additional to the Velox incorporating gas-turbines have been described. The Sural boiler has been installed<sup>140</sup> in two French battleships and a number of torpedo boats. Combustion of oil is carried out at 2 atm.-pressure in a water-tube boiler, the combustion gases from which pass through gas-turbines which in turn drive the air compressors.

The "Equipression" boiler has been installed<sup>141</sup> at the Arrighi power station in Paris and develops 1200 kw. The fuel is oil, although it is said that pulverised fuel can be used, and is burnt at about 80 atm.

in a very compact boiler and the combustion gases again pass to a gas turbine which together with a steam-turbine operated by the boiler steam drive the generator. The combustion air is compressed by internal-combustion piston engines. Complicated arrangements are provided to ensure heat conservation by maximum interchange. An over-all efficiency of 42% is claimed. A 15,000 kw. set is to be manufactured on the same lines.

*Pulverised fuel firing.*—L. T. Work has given<sup>142</sup> a short review of the papers published in 1947 on particle size measurement, types of mill, classification, and grindability. Further details of the Blaw-Knox pulveriser have been published.<sup>143</sup> The development of a meter for flowing mixtures of air and pulverised fuel has been described.<sup>144</sup> An accuracy of  $\pm 5\%$  is claimed.

The development and present design of pulverised fuel-fired central electric-power stations are outlined by T. Smeaton.<sup>145</sup> F. H. Reynst has described,<sup>146</sup> in general terms, means for inducing resonant vibration during the combustion of pulverised fuel in order to increase the scrubbing action between the particles and the gases. The distribution<sup>147</sup> of pulverised bituminous coal by road and rail tank cars is being undertaken in Great Britain. The fuel is discharged by gravity aided by compressed air. The German industry concerned with pulverising brown coal and storing and distributing the dust has been described<sup>148</sup> in a very detailed report. The necessary safety precautions are given. Where plants in Pennsylvania are suitably located, cheap anthracite fines are being burnt<sup>149</sup> successfully in admixture with bituminous coal in rotary cement kilns.

The importance of the application of appropriate instrumentation and automatic control to pulverised fuel plants has been stressed.<sup>150</sup> It is concluded that such equipment is an essential part of the plant and not merely an accessory, if increased thermal efficiency is to be obtained.

#### *Boiler slags, deposits and corrosion*

*Slags.*—W. Gumz has reviewed<sup>151</sup> the published information on the behaviour of the mineral constituents of coal during combustion. Zinzin's, Selmangs', Endell's, and Werners' classifications of ash characteristics are described. German experience of the behaviour of coals with ashes up to 30% has been reported<sup>152</sup> and the influence of the various components of the ash is indicated.

*Deposits.*—H. E. Crossley has given<sup>153</sup> further details of the work of the Boiler Availability Committee. Reference is made to the complete immunity of pulverised-fuel boilers from troubles due to phosphorus in the coal and the relative immunity to corrosion due to sulphuric acid. Laboratory work showed that the conditions necessary for the volatilisation of phosphorus from coal, i.e., high temperatures and absence of oxygen, were unlikely to apply to the combustion of pulverised-coal. In another paper<sup>154</sup> details are given of work on the reduction of  $\text{SO}_3$  by constituents of boiler-flue dust. It is shown that the immunity of pulverised fuel boilers to sulphur troubles may be partly due to the presence of fly ash particles rich in  $\text{Fe}_3\text{O}_4$  which reduces  $\text{SO}_3$  to  $\text{SO}_2$  above 500° c. Coke, another constituent of fly ash, was also found to be active

in reducing  $\text{SO}_3$  to  $\text{SO}_2$ . It is suggested that coke or the magnetic fraction of flue dust might be used to reduce the  $\text{SO}_3$  in the flue gases by injection into stoker-fired boilers.

*Corrosion.*—The behaviour of cast iron and steel under corrosive attack from sulphurous gases in boilers are compared by J. R. Jenkinson and J. R. Rylands.<sup>155</sup> Cases of internal corrosion of water tubes are described.<sup>156</sup>

*Industrial furnaces.*—J. H. Slater reports<sup>157</sup> that conversion of a low pressure blast-furnace to high pressure operation increased iron production and the coke to iron ratio decreased by 13%. Flue dust production also decreased. A summary has appeared<sup>158</sup> of the use by the Germans of carbon linings for blast furnaces. M. T. Cory and F. B. Thacker<sup>159</sup> regard a combination lining of carbon and fireclay brick as better than either an all carbon or all ceramic. R. Guthmann has reviewed<sup>160</sup> German experience in the use of pulverised fuel for carburetting in gas-fired open-hearth furnaces and American experience with wholly pulverised fuel-fired open-hearth furnaces.

A thorough investigation of German furnace design is reported.<sup>166</sup> No novelties were found, but constructional standards were on a high level. The problem of working furnaces at temperatures below  $850^\circ\text{C}$ . is discussed by E. Watkinson.<sup>162</sup> Dilution of the combustion products by recirculation of flue gas is recommended and the beneficial effect on thermal efficiency noted in a number of industrial applications such as a direct coal-fired air heater, a coke-fired foundry mould, and a direct gas-fired lacquer baking oven.

There is much interest in the use of oxygen enrichment in the iron and steel industry. D. D. Howat concludes<sup>163</sup> from an analysis of results obtained in Germany, Russia and elsewhere that the use of oxygen in blast-furnaces reduces fuel consumption but brings operating trouble with bridging and hanging and unless oxygen can be produced for 6d. per 1000 cu. ft. there will be no economic advantage. German experience with the use of oxygen in blast-furnaces is described,<sup>164</sup> but the economic advantage is not assessed. M. W. Thring considers<sup>165</sup> oxygen would be an economic proposition if applied to special cases such as in the production of ferromanganese. In the open-hearth furnace oxygen is stated to be only of interest in the "critical period" of the melt and when introduced in such a way as to improve mining and combustion conditions. In a later paper he adds<sup>166</sup> that oxygen in the Bessemer process enables more metal scrap to be consumed and the operation is speeded up. G. V. Stottman has given<sup>167</sup> an account of American experience with oxygenated-oil-firing and the use of oxygen as a bath-reagent. Some 20 furnaces have been equipped for the former. The effect varies with the furnace, the greatest improvements being obtained in small furnaces of the older types. When oxygen is added to the bath, the refining period in the production of low carbon steel is shortened. Trouble with refractories is reported<sup>168</sup> where oxygen is used in open-hearth furnaces. The results of a series of experiments with oxygen in a cupola are reported.<sup>169</sup> It was concluded (1) that the output of the cupola was a function of the degree of oxygen enrichment, (2) the fluidity of the metal was greater than with air, (3) there was decreased iron in the slag, and

increased silicon and manganese in the metal but less sulphur; carbon was unchanged, and (4) coke consumption was decreased.

*Non-industrial heating and cooking.*—R. F. Dufton has described<sup>170</sup> the results of experimental investigations into the heating requirements of houses heat-insulated to various standards. Eight houses insulated to four different standards were first tested in an unoccupied condition and subsequently during occupation by tenants who were not specially selected in any way. The investigation showed that expenditure on heat insulation up to £60 per house was reasonable in view of the resultant heat saving. These experiments have now<sup>171</sup> been extended to a further 20 houses identical in size, design and thermal insulation but with different methods of heating.

R. H. Rowse has described<sup>172</sup> the work being done in Great Britain on domestic heating research. A series of agreed performance standards for solid fuel appliances has been drawn up and appliances receive Government approval if the tests are satisfactory. Provision has also been made for more complete testing of appliances by the erection of special calorimeter rooms.

German domestic solid fuel appliances have been described<sup>173</sup> as also a new American heating unit, the Anthratube.<sup>174</sup> The latter is a complete boiler burner unit for anthracite which is fed into the upper end of an 18 in. long water jacketed-tube in which it burns. High efficiencies are claimed. A Report has recently been issued<sup>175</sup> describing American war-time research on the practical utilisation of solar energy principally for house heating. Very satisfactory results were obtained from a series of partially blackened overlapping glass plates mounted on a roof. Air passing between the plates is supplied to the house. On a bright day the efficiency of collection of solar energy was 35–40%.

*District Heating.*—The Second Report of the District Heating Committee has been published.<sup>176</sup> Recent reports from various sources are reviewed and the economics of the Dundee scheme discussed. Reference is made to the claim that the standard of heating provided by district heating is much higher than that hitherto obtained by conventional methods of heating and to the influence of district heating on the gas industry. A preliminary account has been given<sup>177</sup> of district heating in America where in many cases it is favoured because operating and maintenance costs are low enough to outweigh the higher capital charges in comparison with separate heating plants for individual houses. Schemes at Virginia and Dayton are described. A thermal-electric district heating scheme for the City of London has been proposed.<sup>178</sup> V. I. Khasilev has derived<sup>179</sup> charts for the determination of the economic and practical feasibility of district heating schemes. Extensions of thermal-electric schemes in Copenhagen are described<sup>180</sup> with full details of power station arrangements, conduits, etc.

*Large-scale hydrogenation.*—Further details<sup>181</sup> have been reported of the origin and preparation of the A.D.5 paste used so satisfactorily as a catalyst support in the hydrogenation plant at Welheim, Germany. It is essentially a bentonite bleaching clay activated by treatment with hydrochloric acid.

*Locomotives.*—A. J. Townsend has described<sup>182</sup> a new type of locomotive boiler giving reduced coal consumption. C. R. H. Simpson has reviewed<sup>183</sup> the directions in which developments in steam locomotives could take place in Britain and discussed methods of achieving improvements. The steam conditions required for steam-turbine locomotives have been established.<sup>184</sup> The first of three 6000 h.p. steam turbine-electric locomotives have been completed<sup>185</sup> in America.

*Pulverised fuel gas-turbines.*—L. Musil has published<sup>186</sup> a small book which discusses amongst other subjects the problems of the combustion of solid fuel for gas-turbines and the simultaneous production of electricity and town's gas with gas-turbines.

A study has been made<sup>187</sup> of the technical problems and costs of operating coal-fired gas-turbines. Whereas it is recognised that the oil-fired gas-turbine, on account of fuel costs, is only likely to find application in power generation for peak loads, the coal-fired gas-turbine may well at central power stations in conjunction with steam plant attain an efficiency equal to that of modern steam plant but at lower capital cost. Where cooling-water is short, the coal-fired gas-turbine will score over the steam-turbine on account of its much smaller dependence on ample cooling. In small sizes for use in factories, the gas-turbine will offer a better ratio of power output to heat than steam plant. It is considered that with open cycle gas-turbines although it may not be possible to prevent the formation of deposits on the turbine blading, the deposits should be capable of removal by washing. F. Münzinger also agrees<sup>188</sup> that coal-fired gas turbines are superior to steam turbines in sizes up to 1500 kw. J. I. Yellott discusses<sup>189</sup> the importance of the coal-fired gas-turbine and its position in industry. Detailed calculations are given for various conditions of power and heat supply from exhaust waste heat.

*Agriculture and horticulture.*—A detailed survey of fuel utilisation in agriculture and horticulture has been prepared by Margarite Yeo.<sup>190</sup>

*Heat-pump.*—The subject of heat-pumps continues to hold interest. E. F. Gill considers<sup>191</sup> that small self-contained air-conditioning units incorporating a heat-pump could be made at a first cost which would be higher than for electric heaters but the economy resulting would warrant installation in private dwellings. W. E. Johnson<sup>192</sup> whilst regarding the possibility of the heat-pump as greater in the home than in industry inclines to the view that installation costs are not warranted. To avoid adding to peak loads, the use of water-storage is recommended.<sup>193</sup> This also reduces the capacity of the plant required. T. F. Thomas has discussed<sup>194</sup> the possibilities of air-cycle heat-pumps.

### Atmospheric pollution

C. F. Brockington estimated<sup>195</sup> that 150 tons of solid deposits fall annually per sq. mile of the West Riding of Yorkshire. The compulsory use of semi-distilled coal is recommended. The Minister of Fuel and Power has given<sup>196</sup> an assurance that in all new coal-burning power stations the most modern methods will be used to prevent pollution of the air by smoke, grit, and oxides of sulphur, as well as of dust from coal-handling. In America, the Los Angeles Office of Air Pollution

Control has reported on the meteorological aspects<sup>197</sup> of pollution and on its irritant effects<sup>198</sup> on various individuals. Pittsburgh has undertaken<sup>199</sup> smoke-control by appointing smoke inspectors and ruling that any type of fuel may be burned as long as it does not cause emission of smoke. There has resulted a tendency to convert to the use of oil and a demand for low-temperature carbonisation fuels. H. B. Lammers has surveyed<sup>200</sup> the sources of smoke and air pollution arising from thousands of fuel-burning plants, in American cities. It is concluded that increased mechanisation is useless without well trained personnel. A smokeless heating boiler has been developed<sup>201</sup> by Bituminous Coal Research and will shortly be on the market and the same organisation is undertaking conversion of the common vertical sectional boiler to smokeless cross-feed magazine type firing. Details have been given<sup>202</sup> of a long-term research at Illinois University to design a smokeless furnace of which the prototype has been constructed. It consists of a coking chamber followed by a coke-burning chamber. The volatile matter released from the green coal mixed with secondary air passes over red hot coke in the coke-burning chamber and combustion is completed in an auxiliary combustion chamber located above the flues. The proportion of smoke produced is comparable with that from an underfeed stoker. For the abatement of smoke from railway locomotives the overfire steam-air jet is considered<sup>203</sup> the most satisfactory. G. Nonhebel has reviewed<sup>204</sup> methods of collecting and disposing of the dust from powdered-fuel boilers and also of the removal of sulphur dioxide from flue gases.

### Fuel economy

The report of a French Commission on Fuel Economy is now available.<sup>205</sup> The use of coal in electricity generation, on railways, in the metallurgical industries and in coke ovens and gasworks is considered. Further development of hydro-electric schemes is recommended and modernisation of existing coal-fired stations. The use of tariffs to smooth the load curve is considered desirable. Electrification of main and suburban lines would save 6-7 million tons of coal. Fuel wastage in forges and foundries is due to poor design of furnaces. More use should be made of insulation. The Belgians have also made recommendations<sup>206</sup> to improve efficiency in casting operations. A study has been made<sup>207</sup> of the firing of British kilns. The fuel losses that arise from inadequate control are illustrated and the advantages of mechanical firing which can result in 10-15% saving in fuel are described. Improvements made in brick and tile kilns are reported.<sup>208</sup> These resulted in a marked decrease in the firing time and a fuel saving of 20%. Fuel economy in coal carbonisation has been reviewed<sup>209</sup> by T. C. Finlayson. Attention is paid to the use of recuperators or regenerators. Coke-oven regenerators in particular have been improved as a result of an investigation which showed the importance of surface area. The gain in efficiency to be obtained from wetting coal used on chain-grate stokers can be substantial<sup>210</sup> and this has been emphasised. The gain depends on the type and size of coal. Load variation can be followed more easily and ash-pit losses are reduced.

K. Rummel has brought<sup>211</sup> up-to-date the handbook of the Verein

deutscher Eisenhüttenleute which gives data of power and heat consumption in every activity of the iron and steel industry. M. W. Thring has reviewed<sup>212</sup> the possibilities of the reduction in fuel consumption in the iron and steel industry and analysed the disparity between theory and practice. Investigations in progress on instrumentation of furnaces and on the rate determining factors in furnace-reactions are described. New developments leading to fuel economy are discussed. The advantages of high pressure, high temperature steam plant in steel mills are emphasised by F. A. Sawyer.<sup>213</sup> Such plant is estimated to lead to 10% fuel saving. American steel-mills are now installing high-pressure plants. H. L. Halstead,<sup>214</sup> in considering the balance of fuel and power in a steel works, thinks that coke-oven gas and tar are fuels which are more advantageously used elsewhere than in the steam and power plant. Blast-furnace gas and coke-breeze should also be utilised to the maximum extent elsewhere and only the balance employed in the steam and power plant. Improved steam turbine loading can result from operating the latter in conjunction with an outside electrical system. J. S. Kerr stresses<sup>215</sup> the value of instrumentation and automatic control at an integrated iron and steel works in order to obtain consistent operating conditions and lowest heat consumptions. At an integrated works the coke-oven gas and blast-furnace gas are insufficient to meet all heat requirements and additional fuel either coal or oil has to be employed. In agreement with Halstead, only surplus blast furnace gas reaches the boilers and deficiencies in fuel thereat are made up with low grade slack, breeze and slurry.

*Heat-balances.*—As a preliminary to overhauling the methods of utilising fuel at a factory, a heat-balance is essential. J. Edward has described<sup>216</sup> the methods of measurement available for this purpose and J. B. Mason and L. Clegg<sup>217</sup> the preparation of such heat-balances in various industries with a view to reaching figures for the “specific fuel consumption” per unit of saleable goods for individual works in those industries. These consumption figures are then analysed taking each item of equipment in the works in turn in order to reach the “economic fuel target” which represents the minimum fuel consumption per unit of production towards which that works should strive to attain. These target figures are not necessarily the same throughout an industry because of the many variables which differ from one works to another.

*Industrial steam peaks.*—E. G. Ritchie has examined<sup>218</sup> the effects of fluctuations in the demand for process-steam on the efficiency of the boiler-house. It is pointed out that if when additional demand for steam occurs, the boiler-house can meet it in any way such as by use of a steam-accumulator, the development of false peaks in demands is often avoided. The methods considered of meeting peak steam-demands are the use of thermal storage, live steam-accumulators, feed water-accumulators, hot process water storage, and exhaust steam storage. Such devices are particularly valuable when process steam and power generation are combined in one works.

*Utilisation of low-grade fuel.*—A. R. Eastcott has described<sup>219</sup> 10 years' experience with high ash lignite and sub-bituminous coals of high moisture content. C. F. Wade recommends<sup>220</sup> the retort or well grate

fitted with primary and secondary air control for the firing of low-grade coals in Lancashire and other shell-type boilers. D. B. Reay has had success<sup>221</sup> with chain-grate stokers after fitting dead plates below the grate.

A system is described<sup>222</sup> of burning coke breeze on a chain-grate stoker in which the deficiency of the coke in volatiles is made up by spraying the bed immediately inside the furnace with oil. The equipment can also be used with high ash coals. The quantity of oil used is some 5% of the fuel. Reference has already been made to the Courtauld steam jet ignition. A full description of the application of the method is now available.<sup>223</sup>

### Analytical methods

Recent developments in the analysis and testing of solid fuel have been reviewed by A. H. Edwards.<sup>224</sup> Methods of taking samples for analysis of consignments of coal are discussed.<sup>225</sup> The use of a probe worked vertically like an auger is described.

An investigation has been made<sup>226</sup> of the normal air drying method of moisture determination as a result of criticism that oxidation occurs. It was found that low-volatile coals were not affected but with high-volatile bituminous coals and sub-bituminous coals there was oxidation with loss of heating value. T. J. Finnegan and H. L. Smith have developed<sup>227</sup> a method of determining the moisture content of coal used in a direct fired pulverised-fuel installation based on the heat balance for the whole plant and the primary air temperature. J. A. Dulhunty discusses methods<sup>228</sup> of determining inherent moisture and describes a method using controlled vaporisation. J. R. Bainbridge *et al.* record experiences<sup>229</sup> in determining the moisture contents of brown coals varying from 36-68% by a distillation method. A direct rapid method of determining moisture by heating the coal in a tube in a stream of nitrogen and passing the gas through a U-tube containing Anhydrone is reported.<sup>230</sup> X-ray absorption has been proposed<sup>231</sup> as a means of determining the amount of ash in coal after suitable calibration of the instrument.

K. Barton and J. Tampa have investigated<sup>232</sup> the determination by recognised methods of the various forms of sulphur in Czechoslovakian brown and black coals. In consequence of the unreliability of these methods, a method for the determination of sulphates and of pyrites is suggested. The Belcher and Spooner method for the rapid ultimate analysis of coal has been tested<sup>233</sup> in comparison with the British Standard method and found satisfactory except in the case of chlorine. T. H. Duffy<sup>234</sup> has given a nomograph based on proximate analysis, sulphur content and heating value which gives total carbon in coal with an accuracy claimed as 0.28%.

When determining the calorific value of coke in the bomb calorimeter, J. Hamaker and M. Rietveld recommend<sup>235</sup> the briquetting of the coke or coal-tar pitch rather than the more usual, sucrose, benzoic acid, etc. L. Sumegi claims<sup>236</sup> to have produced formulae for gross and net calorific value of coal based on analysis which are better than the Dulong and other formulae.

The expressions are:

Gross calorific value =

$$81 (C - 0.74 O_{\frac{1}{2}}) + 345 (H - 0.125 O_{\frac{1}{2}}) + 25S \text{ and}$$

Net calorific value =

$$81 (C - 0.75 O_{\frac{1}{2}}) + 285 (H - 0.125 O_{\frac{1}{2}}) + 25S - 6M$$

where the symbols represent the percentage of the elements and M the moisture in the coal. The formulae are not applicable to lignites.

A method for determining together the sum of the phenolic and carboxyl groups in humic acids, lignins, etc., by the amount of chemisorbed  $Ba(OH)_2$  is reported.<sup>237</sup> The carboxyl group is then determined separately by chemisorption of calcium acetate and the phenolic group found by difference.

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# MINERAL OILS

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**A**LTHOUGH great progress has been made in the various activities of the oil industry, including more recent geo-physical methods of prospecting, the great variety of means of reaching oil formations and the ever-increasing importance of methods of increasing oil production, yet it is safe to say that mineral oil is a wasting asset and therefore the need to make available every so-called residual and hitherto unwanted products of production and refining is all the more urgent. Primarily amongst these are natural gas and cracked gas.

Actually, a new industry based on petroleum is rapidly taking shape—the production of chemicals, solvents, and intermediates in the chemical industry, as we know it to-day. So much is this the case that already many developments are imminent. New refineries in the U.K. and other user-centres are foreshadowed and extensions planned to existing installations.

A generation ago the idea was universally accepted that the refining of petroleum is best achieved at or near the source of production. By this means losses are not carried in expensive transport and the various primary commodities—gasoline, kerosine, intermediate oils, lubricants and bitumen—could be classified at the centre of operations and despatched to their ultimate markets. In fact, the crude oil was best handled at the very beginning. The impact of widespread cracking materially altered this attitude. When as much as 30% of a raw material is turned into gas it is clear that unless means are provided for its utilisation on the spot serious losses such as flares and other forms of wasteful disposal are inevitable. And so it comes that the centre of gravity of the refining industry has shifted to the consuming end where the losses in cracked gases can be more readily made good by their conversion into products immediately useful. Wherever a refinery is set up there will be supplies available for the newest and latest chemical industry. Consequently, in this review emphasis will be laid on the development of chemical entities derived from mineral oil.

At the outset it should be pointed out that the petroleum industry flourished (and up to a point, still does) on the production and marketing of simple groups of derivatives fractionally distilled from the native crude, gasolines, white spirits, kerosines, gas oils, and lubricants. The remarkable progress that has been discussed in these Annual Reports for many years is due to a change of attitude that began about 1918, at the end of the first world war.

Organised scientific effort was the cause. New research organisations sprang up and a new personnel appeared with a university background. These newer laboratories and staffs still have vast opportunities since

exact knowledge of the components of mineral oil hardly extends beyond the gasoline range in which about sixty individual entities have been identified—a few naphthalene derivatives in kerosine and some long-chain paraffins in the solid waxes. On the other hand, physical data is being steadily accumulated and the study of economically important reactions such as isomerisation, alkylation, polymerisation, and pyrolysis is making rapid progress.

A paper of fundamental importance on pure compounds from petroleum by D. Rossini<sup>1</sup> summarises the work developed in co-operation with the American Petroleum Institute and deals with the investigations carried out at the National Bureau of Standards on the separation of definitive entities occurring in petroleum.

Again of general interest to the chemist is the survey afforded by R. P. Russell,<sup>2</sup> in which particular descriptions are given of catalytic cracking and hydrocarbon synthesis from mineral oil such as lubricant additives, resins, detergents, and weedkilling hormones. It was stated that *all* the organic materials (including rubber and alcohol) needed to supply the world requirements for a year could be met from a 10-days' production of crude oil.

A useful summary of the work in progress at the Manchester Oil Refinery<sup>3</sup> contains a section on new products from petroleum.

E. R. Smoley, R. M. Torrey, and J. Kniel<sup>4</sup> give a general survey for the derivation of chemicals from petroleum, based on cracking for the production of olefins. In 1946, chemicals from petroleum amounted to  $4 \times 10^9$  lb. Actually from mineral oil 50% of the ethanol, 100% of isopropyl alcohol, 75% of the acetone and 90% of the amyl alcohol are being produced at the moment. Synthetic detergents amount to 100,000 tons/year.

Referring to the synthetic aliphatic industry, H. B. McClure and R. L. Bateman<sup>5</sup> indicate that interesting developments in the U.S. from petroleum sources are concerned with triethylene glycol, 2-methyl-2:4-pentane diol, 2-ethyl-1:3-hexanediol, polyethylene glycols, chlorinated kerosine fractions, dichloropropylene, and isobutylene.

A further article<sup>6</sup> shows that petroleum is now becoming the principal source of the total aliphatic chemicals made in the U.S. The various types of reaction applied to hydrocarbons are detailed, in particular dehydrogenation, chlorination, and oxidation. From coal, acetylene together with "synthine" are the main derivatives.

Describing chemicals from petroleum and natural gas G. Egloff<sup>7</sup> points out that hydrocarbons available for processing range from methane to high molecular weight compounds, are all obtainable from cracked gases and liquid petroleum fractions. Alkylation produces compounds suitable for chemical manufacture. Polymerisation of olefins gives products varying from dimers to solid multipolymers. Detail of the synthesis of alcohols, aldehydes, ketones, acids, edible fats, glycerol, chloro-derivatives, plastics, rubber, and insecticides is afforded. Ten million lb. cresols were produced in 1945 and 30 million lb. of naphthenic acids. The Fischer-Tropsch synthesis should produce 160 million lb. of acids, ketones, and aldehydes per year. Further, synthetic edible fats are to be obtained from hydrocarbon waxes, combined with the synthetic glycerol (ex

propylene). It is expected that 35 million lb. of glycerol will be produced per annum. As incidental by-products Egloff names insecticides, elemental sulphur, and ammonia. Reference may be made to a further paper by the same author.<sup>8</sup>

Another account of the materials yielded by petroleum halogenation is afforded by Egloff.<sup>9</sup> Such products include insecticides, soil fumigants, weedkillers, anaesthetics, soporifics, refrigerants, heat-exchange and anti-freeze compounds, rubbers, resins, plastics, solvents, anti-knock compounds, and chlorinated paraffin waxes.

A very large plant for production of glycerol will soon be in operation, and the commercial manufacture of nylon from *cyclohexane* (replacing some hydrogen by chlorine) is now contemplated.

Actually the large-scale manufacture of glycerol has now materialised, and it is estimated that 20% of the U.S. requirements will be met. The project is based on the well known Shell Company's researches in which the sequence propylene  $\rightarrow$  allyl alcohol  $\rightarrow$  dichlorohydroxypropane  $\rightarrow$  glycerol is followed.<sup>10</sup>

The present demand for aromatic hydrocarbons can only be met by an ever increasing production from petroleum. Progress between the two world wars as far as toluene is concerned has been reviewed by Howes, from the aspects of azeotropic and extractive distillation.<sup>11</sup>

Petrocarbon Ltd. has been formed to acquire the rights of the Caterole process in which the lower petroleum fractions are cracked over a metallic catalyst at *ca* 630°–680° C.<sup>12</sup> and produce olefinic gases and liquid aromatic hydrocarbons.

A general review of the production of aromatics from petroleum and the elucidation of the principles involved are given by H. Steiner.<sup>13</sup> Dehydrogenation, cyclisation, isomerisation, hydroforming and high-temperature cracking are discussed in detail. The chemical reactions occurring in these processes are outlined and a recently developed method using dehydrogenation catalysts for the production of aromatic hydrocarbons together with low molecular weight defines is described (the Caterbe process, *q.v.*). Amongst the higher aromatic hydrocarbons isolated are chrysene, pyrene, benzanthrene, fluoranthene, and 3:4-benzfluorene. Aromatic hydrocarbons are equally subject to the alkylation reaction and a large variety of catalysts has been put forward. For example, benzene has been converted into toluene with dimethyl ether in the presence of phosphoric acid.<sup>14</sup>

Another general review is afforded by R. F. Goldstein<sup>15</sup> in which the manufacture of butadiene is discussed from the starting out materials alcohol and petroleum. Glyoxal and thiophene are now manufactured from mineral oil.

A discussion of the fatty acid situation in Germany during the war has appeared.<sup>16</sup> The output approximated 100,000 tons/year. In the Ruhr Chemie process, wax was heated with nitrosyl-sulphuric acid in the presence of "nitrous gases" (8% NO<sub>2</sub>). Fifty per cent. of the wax was oxidised. In the Witten plant potassium permanganate (0.1–0.2%) was the catalyst and air the oxidant. The acids produced were suitable after purification for soap and margarine manufacture.

The manufacture of ethyl alcohol from petroleum is described by R. S. Aries.<sup>17</sup> The direct hydration of ethylene is exothermic and equilibrium is favoured by low temperature and high pressure.

At 200° c. and 21 kg./cm.<sup>2</sup> equilibrium corresponds to 20% EtOH and catalysts (*e.g.*, silver sulphate) are required to accelerate the reaction.

B. H. Weil,<sup>18</sup> in an article on detergents from petroleum affords a general review of this field with special emphasis on those produced from mineral oil. Fifty references to recent work are given.

On the same subject<sup>19</sup> it is suggested that petroleum will yield 500 million pounds weight/year by 1949 mainly as alkyl sulphonates and alkylaryl sulphonates.

Furthermore, P. R. Stedehonder, P. W. O. Wigga, and H. F. Dammers<sup>20</sup> point out that fatty acid soaps are being largely replaced by synthetic detergents, such as secondary alkyl sulphates and alkylaryl sulphates derived from the olefins produced in the cracking operation.

The catalytic oxidation of paraffin wax yields products similar to fatty acids that are available for soap making or for edible oils.

### Alkylation, polymerisation and synthesis

Alkylation and related processes are still responsible for informative communications. Thus F. C. Whitmore<sup>21</sup> discusses the formation and reactions of carbonium ions. This conception is used to explain various rearrangements, interchanges, acceptances, and migrations. In particular, examples are given of isomerisation and dimerisation of olefins, alkylation, etc.

The alkylation of *isoparaffins* with olefins in the presence of sulphuric acid is the subject of a paper by F. Norton and A. R. Richards.<sup>22</sup> It was shown in the original communication relating to alkylation<sup>23</sup> that the various trimethyl pentanes stirred with 97% sulphuric acid yielded mixtures of hydrocarbons whereas 2:2-dimethylbutane and 2:2:3-trimethylbutane were not attacked. There is still considerable difficulty in elucidating the complex mechanism of the alkylation reaction but, at the moment, it is suggested that there must be an intermediate formation of an *isoparaffin-olefin-catalyst* complex which by the migration of methyl groups produced by the cleavage of the carbon-carbon bonds in the *isoparaffin* fragment leads to the building up of the ultimate reaction products. The earlier views put forward<sup>24</sup> are still cogent.

The use of zinc alkyls in the preparation of hydrocarbons with a quaternary carbon atom<sup>25</sup> is discussed by the Oxford workers. This very important paper by J. C. Smith and his collaborators summarises a long research into the synthesis of hydrocarbons containing quaternary carbon atoms. Zinc alkyls afford high yields of a range of material from *neopentane* to 1:2-diethylcyclohexane. Details are given of the preparation of high boiling products incidental to these syntheses such as 1:3-dimethyl-4-*tert*butylbenzene. A selected bibliography is given.

A further contribution to the chemistry of petroleum and its derivatives in which attention is drawn to the use of modern high-efficiency fractionation is also due to J. C. Smith and his colleagues.<sup>26</sup> For example, use of a 100 theoretical plate column brought about the separation of

a fraction from Oklahoma kerosine having b.p. 145–146° 5/56 mm. which solidified and was, in the main, 2-methylnaphthalene.

A number of papers are concerned with polymerisation. Polythene<sup>27</sup> is now manufactured from ethylene by the impact of pressure *ca.* 1000 atm. and at temperatures around 200° c. and is chiefly used as an insulating material for radar and submarine cables.

The molecular weight of the product may be of the order of 50,000 containing 4000 linked carbon atoms. The entire range of synthetics includes plastics, tough or brittle waxes, soft waxes, pastes, and greases. Crystallisation in waxes, and polymers and interpolymers is correlated with chemical structure. Norrish and Russell<sup>28</sup> have shown that the velocity of polymerisation of *isobutene* in the presence of boron trifluoride can be estimated at as low a temperature as –140° c. Measurable rates are also obtained with stannic chloride as catalyst at –78.5° c. There is no reaction when water is absent. A mechanism is suggested involving a chain reaction initiated by charged ions derived, for example, from hydrated stannic chloride.

The effect of fluorine compounds in polymerisation reactions is considered by Topschiev and Panskin.<sup>29</sup> Compounds of boron trifluoride carry the polymerisation of low molecular weight hydrocarbons further than do sulphuric or phosphoric acids—a reaction accompanied with some cyclisation. The boron trifluoride compounds with the greatest activity possess hydroxyl-containing molecules.

The lower olefins at 150 atm. and 20° c. yield products within the lubricating oil range but even at –20° to –80° c., *isobutene* gives high molecular weight bodies suitable as lubricating oil additives.

An interesting communication by Challenger and his colleagues<sup>30</sup> is concerned with the substitution and polymerisation reactions of thiophen and the thiophthenes. Thiophen is polymerised by anhydrous ferric and stannic chlorides yielding amorphous (impure) solids. Solid thiophthen (thiopheno-2': 3'-3 : 2-thiophen) gives dihalogen and dinitro derivatives. Polymers are produced by means of hydrogen bromide or phosphoric acid.

Butane isomerisation by the Universal Oil Products Company process<sup>31</sup> is concerned with the application of an aluminium chloride catalyst on an inert packing. Activity is maintained by continuous introduction of aluminium chloride.

The catalytic dehydrogenation of ethylbenzene<sup>32</sup> is brought about by means of a catalyst containing Cr<sub>2</sub>O<sub>3</sub> (70%), Al<sub>2</sub>O<sub>3</sub> (15%), and Cu (15%). A yield of 48.5% of styrene at 600° c. was achieved. Incidentally, it is claimed that a lumina deposited on kaolin gave a 92% conversion of alcohol to ethylene at 420° c.

A considerable amount of work has been accomplished on the combined dehydrogenation and cyclisation of paraffin hydrocarbons containing chains of six or more carbon atoms. Aluminium chloride<sup>33</sup> brings about dehydrogenation followed by cyclisation. And a range of contact materials available for such purposes appears in the literature ranging from bauxite, alumina containing vanadium, antimony, or molybdenum, as well as metals such as cobalt, copper, chromium, iron, manganese, nickel, tungsten, and silver.

Chromium oxide is put forward as a catalyst promotor for the Fischer-Tropsch synthesis.<sup>34</sup> The incorporation of  $\text{Cr}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  with a  $\text{Co-Cu-ThO}_2$ -Kieselguhr catalyst materially assists the operation.

In a description of the Phillips butane dehydrogenation process<sup>35</sup> the authors detail a process for the catalytic dehydrogenation of butane over a chromium-aluminium catalyst at  $1100^\circ\text{F}$ . Similarly, K. Hachmuth and G. H. Hanson<sup>36</sup> discuss, in general, the catalytic dehydrogenation of butane to the normal butylenes.

## Refining

There are no outstanding developments to be chronicled for 1948. Improvements have to be reported, particularly in cracking technique and in desulphurisation.

As far as cracking is concerned, considerable progress has been made, quite empirically, in the direction of catalysis. Cracking to-day is not merely the violent impact of high temperature and pressure on simple hydrocarbon molecules; it has become, rather, a modified change under the influence of a large variety of contact materials in the quasi-fluid condition. True it is that "catalytic cracking" profoundly modifies the customary products of the older and more familiar thermal pyrolysis. As far as higher octane-number spirits are concerned it is true that an invaluable contribution to petroleum technology has been achieved. The concomitant increase and utilisation of gas products has been already discussed.

In a paper concerned with suspensoid cracking C. H. Caesar<sup>37</sup> shows that over a period of 6-7 years a process has been devised especially suitable for small refineries. The catalyst (2-3 lb./barrel/feed) is used in the form of a slurry and functions in the conventional thermal cracking chamber in place of a special reactor.

Esso's fluid catalyst for the Fischer-Tropsch synthesis<sup>38</sup> has introduced considerable economies in plant and operating costs. Partial oxidation of natural gas will provide the raw material and further the finely powdered iron catalyst assists in the distribution of the high heat of reaction. The mildly treated gasoline has an octane number of 80, and can be produced at a competitive price.

A patent issued to the Standard Oil Development Company<sup>39</sup> claims that hydrocarbon oil when cracked in presence of a catalyst gives a fraction (A) of b.p.  $90-180^\circ$ , a fraction of b.p.  $70-120^\circ$ , which is solvent-extracted to give an aromatic fraction (B), and a fraction of b.p.  $15-90^\circ$ , which is alkylated with an isoparaffin ( $iso-\text{C}_4\text{H}_{10}$ ) to yield a fraction which is combined with A and B to form aviation gasoline. This has now become almost current practice. To-day's aviation spirit is no longer a straight run spirit, but a blend of isoparaffins, solvent-extracted aromatics, and alkylates such as is described by Howes<sup>40</sup> where feed stock consisting essentially of  $\text{C}_4$ -hydrocarbons with a substantial proportion of  $\text{C}_4\text{H}_8$  is (a) isomerised on a synthetic  $\text{Al}_2\text{O}_3\text{-SiO}_2$  catalyst in presence of steam to convert  $n$ - into  $iso-\text{C}_4\text{H}_8$ , (b) polymerised (dimerised), (c) hydrogenated, and (d) fractionated to isolate the dimeric products. A preliminary polymerisation may precede the treatment of the residual  $n-\text{C}_4\text{H}_8$ -rich fraction by the above process.

Naturally by debutanising and superfractionating  $C_4$ - $C_6$  cuts and further from a  $C_7$  cut after solvent extraction there arise a series of fractions from straight-run spirit of high potential octane performance.

Again, A. G. Arend,<sup>41</sup> in a paper on recent advances in high octane fuel production, gives a description of fluid catalytic cracking, thermofor cracking and the hydrogen fluoride method of alkylation.

E. J. Dunstan,<sup>42</sup> discussing modern trends in oil refining indicates developments in close fractionation, cracking, reforming, desulphurisation, and solvent extraction. New processes have added to the number of by-products which, in turn, have aided the derived chemical industry.

A comprehensive survey of modern refining operations is afforded<sup>43</sup> in a detailed account of forty four leading refinery processes with flow sheets. These comprise fluid, thermofor, *cycloversion*, Houdry, suspensoid, and thermal cracking, alkylation with both sulphuric and hydrofluoric acid catalysts, reforming, desulphurisation, sweetening, solvent treating and dewaxing.

P. C. Weinert and G. Egloff<sup>44</sup> describe three types of works unit concerned with catalytic polymerisation and its commercial application. It is essential that water must be present in the feed to prevent the catalyst being dehydrated.

## Desulphurisation

The main direction in which work on desulphurisation has proceeded lies in the attempt to procure the highest octane number from a leaded fuel.

Thus A. Fookson and A. D. Bell<sup>45</sup> indicate that the problem of sulphur content is becoming increasingly serious due to the depletion of crude oils low in sulphur; consideration must, therefore, be given to the utilisation of reserves, much of which have a high sulphur content. Major objections to the presence of sulphur in gasoline are that the oxidation products are corrosive and the octane number and lead response are adversely affected. The various sulphur compounds which may be present are listed, and methods of analysis for both total sulphur and the different sulphur compounds are described.

An equation is given relating the reduction of lead response to the amounts of sulphur compounds present in the gasoline. Engine wear is directly related to the sulphur content. A very extensive bibliography relating to this problem is given.

The catalytic desulphurisation of high sulphur stocks by the cobalt molybdate process is described by C. Berg, W. E. Bradley, R. I. Sturton, R. G. Fairfield, C. B. Leffert, and J. H. Ballard.<sup>46</sup> This process is applicable to crudes containing 5% or more of sulphur. The conversion of thio-derivatives by contact with the catalyst in the presence of hydrogen to yield hydrogen sulphide brings about effective desulphurisation.

The desulphurisation and reforming of naphthas is detailed by C. J. Helmers and G. H. Brooner.<sup>47</sup> Bauxite is used as a catalyst under vapour phase conditions. A higher operating temperature (950-1050° F.) is needed for reforming as opposed to desulphurisation (650° F.). An increase of 10 to 20 octane rating is claimed in the reforming operation. This paper is of interest because bauxite was proposed as a desulphurising

catalyst many years ago by A. E. Dunstan, F. B. Thole, and F. G. P. Remfry.<sup>48</sup>

For the desulphurisation of higher boiling distillates a paper by K. W. Schneider and H. Feichtinger<sup>49</sup> may be consulted. Solvent extraction has always been an alternative method of removing the polar thio-derivatives from petroleum fractions and of course the well known acid treatment is merely solvent extraction complicated by undesirable side reactions.

Of general interest to refiners is an article on special steel for the petroleum industry by R. Jackson and R. J. Sargent.<sup>50</sup> This communication reviews the major factors operative in the selection of special steel for the oil industry. Heat and corrosion resisting properties are improved by the addition of alloying elements. The increasing importance of high quality castings based on the application of radiographic examination is stressed.

### Analysis and testing

Great credit must be given to the two important standardising bodies—the American Society for Testing Materials [Committee D.2] and the Institute of Petroleum through its Standardisation Committee for their efforts at co-operation. These two bodies have always worked in complete harmony, and it is very gratifying to report that two meetings of the Institute of Petroleum Standardisation Committee have been attended by delegates from the A.S.T.M. D.2 Committee.

It is obviously important that the close relations that have grown up between the Institute of Petroleum and the A.S.T.M. should be maintained and even further developed, and that ultimately there may be a joint publication in the English language of a composite publication on standard methods of testing petroleum and its products, applicable to and essential to all users of mineral oil the world over.

To an increasing extent the testing laboratory is becoming an annex to the physical department in a modern petroleum refinery or research station.

Ever-increasing use is being made of new developments in physics, notably the electron microscope, Raman spectroscopy and the mass spectrograph.

In connection with electron microscopy application and its use in the petroleum industry, S. G. Ellis<sup>51</sup> deals with the construction, use, and maintenance of the electron-microscope. The author points out that the main use of this instrument is for the study of details in specimens of the order of 200 Å. to 10 Å. which cannot be observed with the optical microscope. This range includes many powders, colloids, and catalysts which are of industrial importance. The problem of specimen preparation and mounting is discussed, a matter of great importance if all the details are to be revealed. The thickness of the specimen is usually less than 1  $\mu$ ; suitable films on to which specimens may be mounted are given. The interpretation of the electron-micrographs requires some experience, because confusion may be caused by the relatively great depth of focus of this instrument. Calibration can be accomplished by using replicas

of diffraction gratings. Auxiliary techniques, such as shadow casting and staining, which increase contrast are described. An extensive bibliography is provided.

Further, in a paper entitled "Oil Industry Uses for Electron-Microscopy" (II),<sup>52</sup> the same author considers the application of the electron-microscope, and gives examples of its use. This instrument has proved useful in the study of soaps and the properties of greases; electron-micrographs of calcium- and sodium- base soaps are reproduced. The methods of specimen mounting, both for direct and shadow micrographs are described. Work which has been done relating the change of structure of calcium and sodium base soaps with shear is outlined. Other electron-micrographs in the text comprise various catalyst structures, and full details of the specimen-mounting technique required to take these is given. The use of the electron-diffraction method is also outlined.

Fenske and his colleagues<sup>53</sup> consider the Raman spectra of hydrocarbons in detail. They present the Raman spectra of 172 pure hydrocarbons and show that this method of analysis is applicable to the qualitative and quantitative estimation of hydrocarbon mixtures. Some nine-component mixtures have been successfully subjected to precise determination. In general, it is suggested, that Raman spectroscopy is best used as a complement to infra-red and ultra-violet techniques. Reference should also be made to a contribution by D. J. Rank.<sup>54</sup>

Mass spectrometer analyses of some liquid hydrocarbon mixtures are afforded by R. A. Brown, R. C. Taylor, F. W. Melpolder, and W. S. Young.<sup>55</sup> A review is given of the application of mass-spectrometer analysis to the determination of  $C_8$  to  $C_5$  hydrocarbons. Practically all the  $C_7$  and  $C_8$  paraffins and *cycloparaffins* may be individually determined, but groupings are necessary for 2:2-dimethylpentane and 2:2:3-trimethylbutane as well as for the various octanes. Again, most of the  $C_8$  *cycloparaffin* isomers must be grouped. Recent advance in spectroscopic analysis and the development of the mass-spectrometer should considerably simplify the analyses of such complex mixtures as occur in alkylation and reference should be made to various applications of infra-red spectroscopy to chemical problems.<sup>56,57</sup>

Spectrographs are given for the lower paraffin hydrocarbons that show the various mass fragments into which the molecules disintegrate.<sup>58</sup>

G. C. Eltenton deals with the study of reaction intermediates by means of a mass-spectrometer.<sup>59</sup> He describes a reaction chamber coupled to a Dempster type mass-spectrometer so that short-lived intermediates can reach the electron beam. The intermediates occurring during the decomposition of methane, ethane, propane, propylene, butane, butylenes, are surveyed semi-qualitatively; hydrogen atoms, methyl, and ethyl radicals were identified.

In a similar way intermediates were detected in low pressure flames: for example,  $HO_2$ ,  $CH_3O$ ,  $CHO$ ,  $C_2H_2$ , and  $CH_3$ .

A few papers have appeared concerned with viscosity. R. N. J. Saal<sup>60</sup> describes his rheological investigations of asphaltic bitumen in connection with its technical applications and concludes that at ordinary temperatures bitumens shows a rheological behaviour according to three types:

- (a) a viscosity independent of shearing stress or time,
- (b) a viscosity independent of stress after a certain deformation,
- (c) a retarded elastic deformability with permanent deformations of a thixotropic character.

The viscosity of solutions of primary alcohols and fatty acids in benzene and in carbon tetrachloride is dealt with by W. J. Jones, S. T. Bowden, W. W. Jarnold, and W. H. Jones,<sup>61</sup> and the authors conclude that after a study of the variations of viscosity with composition, none of the relationships proposed for the viscosity of a mixture of liquids affords a proper representation of fact.

A very convenient microviscometer is described by E. Glynn and L. Grunberg.<sup>62</sup> Up to 80 mg. of material are needed and the accuracy claimed is of the order of 0.5%. The method is particularly suitable for opaque liquids.

A physical method of some importance, and largely neglected is the determination of the heat of wetting. Attention therefore may be directed to a paper by I. W. Mills<sup>63</sup> on the prediction of activity of cracking catalysts from their heat of wetting. The author suggests that the heat of wetting by methanol is a measure of the activity of cracking catalysts. Many years ago an assay of the value of bauxite as a desulphurising agent was based on the heat of wetting of the mineral gel with kerosine.<sup>64</sup>

The development of tests for determining rich mixture performance in aviation fuels is described by W. A. Howes and R. Stansfield<sup>65</sup> in considerable detail. The development of improved engine-test methods for the determination of anti-knock rating is emphasised—this involved research on the anti-knock value of various types of hydrocarbon. A description is given of the American C.R.C.F.<sup>4</sup> method of test, now in extensive use. The authors recall that in 1939 there was practically no production of 100 octane number fuel in Abadan, whilst in 1945 the output rose spectacularly to 1 million gallons per 24 hours. All the spirit was produced from the benzine fraction of the crude, there being no catalytic cracking facilities at that time. Useful tabular matter indicates the blending values of a number of aviation-fuel components and of pure hydrocarbons in the aviation-spirit range.

The knock characteristics of 16 pure gaseous hydrocarbons are correlated by Frey and his colleagues.<sup>66</sup> Their relative performance numbers from 60 to 300 may be surveyed in comparison with molecular structure but no generalisations can be made as yet. Isomeric compounds may vary considerably in knock tendency whereas stereoisomers show no significant differences. Olefins may be better or worse than the corresponding paraffins and their performance is greatly influenced by engine conditions.

R. O. King<sup>67</sup> continues his researches on the oxidation, ignition and detonation of fuel vapours and bases. In this section of his work he brings forward further evidence to support the view that the oxidation of hydrocarbon fuel is a heterogeneous reaction.

The anti-knock effect of metallic dope is attributed to the catalytic

action of the surface in the oxidation of the fuel. The surface is maintained in an oxidising atmosphere by continual deposition thereon of the metal of the dope.

In Part IV<sup>68</sup> he shows that the occurrence of non-occurrence of detonation depends on the result of a race between pyrolysis and a heterogeneous oxidation reaction.

A series of communications concerned with processes in the oxidation of hydrocarbon fuels, A. D. Walsh<sup>69</sup> develops a theoretical treatment concerned with chain reactions involving free radicals as carriers.

Naturally, in these days, when the olefin content of cracked gases plays so great a part in the new petroleum synthetic chemistry it is of considerable importance to provide an adequate assay. A number of papers are concerned with the fulfilment of this need. H. C. Rampton<sup>70</sup> describes in some detail the hydrocarbon-type composition of cracked gasolines. He points out that a method of hydrocarbon-type analysis has been developed for cracked gasolines and similar products which permits the determination of groups of hydrocarbons :

- |                |                                  |
|----------------|----------------------------------|
| (a) Aromatics. | (d) Alkenes (non-cyclic olefins) |
| (b) Naphthenes | (e) Cyclenes (cyclic olefins)    |
| (c) Paraffins  |                                  |

The quantity of individual members of each of these hydrocarbon groups can be assessed in most cases since the analyses are carried out on highly fractionated cuts of selected boiling point range.

The procedure of the method has as its basis the following scheme :

- (a) Separation of naphthenes and paraffins from olefins and aromatics by selective adsorption followed by naphthene and paraffin determination on fractions of selected boiling point range.
- (b) Hydrogenation of original cracked gasoline to convert olefins to paraffins and naphthenes without hydrogenation of the aromatic hydrocarbons.
- (c) Determination of the aromatic hydrocarbons on fractions of selected boiling point range prepared from the hydrogenated cracked gasoline.
- (d) Removal of aromatics in hydrogenated cracked gasoline by selective adsorption followed by paraffin and naphthene determination on fractions of selected boiling point range.
- (e) Estimation of alkenes and cyclenes from differences in the analyses of corresponding boiling point range fractions in (a) and (d).

Discussing the determination of olefins in cracked gases, G. E. Mapstone and P. Beckmann<sup>71</sup> indicate that the usual method of the determination of olefins is complicated by the solubility of paraffins in concentrated sulphuric acid. The authors recommend a modified procedure in which total olefins are determined by absorption in the mercuric sulphate-dichromate-sulphuric acid reagent.<sup>72</sup> Another sample is treated with 87% sulphuric acid followed by the mercuric sulphate-dichromate-sulphuric acid, the loss in this latter adsorption gives the residual ethylene content. The higher olefin content is the difference between total olefins and ethylene.

A simple chemical analysis of *isobutene* in binary mixtures with other olefins is described by J. P. W. Hontman.<sup>73</sup> Binary mixtures of *isobutane* with butene-1, butene-2-*isobutene*, and butadiene are determined using hydrochloric acid as reagent in the Bunte gas analysis apparatus.

A very comprehensive paper on the solid state properties of petroleum waxes in terms of composition is afforded by S. T. Minchin<sup>74</sup> in which an account is given of the various physical properties of waxes, and in particular hardness. A useful discussion is incorporated.

## Lubrication

More and more importance is being given to the purely physical aspect of lubrication, thus R. Stansfield and J. C. Cree,<sup>75</sup> discussing lubricating oil testing in engines, conclude that an increasing use is being made of bench tests of oils and an account is given of standard tests in a high-speed Diesel and a petrol engine respectively. It is pointed out that the difficulty of correlating engine performance with the usual laboratory tests is very real and there is definite need for a recognised series of lubricating oil tests in engines specially built and designed for the purpose.

The Cambridge school in a series of papers is concerned with the importance of chemical attack in the lubrication of metals. F. P. Bowden<sup>76</sup> holds that, contrary to the generally held belief that boundary lubrication by long-chain fatty acids, for example, is due to an oriented layer of molecules adsorbed at the surface, such an explanation is an over-simplification. The action of fatty acids on lubricated metal surfaces bears some resemblance to that of the so-called "extreme pressure" lubricants since chemical attack of the surfaces is important.

In the case of the lubrication of metals by compounds containing chlorine, J. N. Gregory<sup>77</sup> considers that compounds containing reactive chlorine atoms can produce on steel surfaces a film of iron chloride which has extremely good frictional properties—and, moreover, will maintain these properties to very high temperature. These lubricating films are only stable in the absence of moisture. And, further, E. B. Greenhill<sup>78</sup> is of the opinion that the lubrication of metal by compounds containing sulphur as with other extreme-pressure lubricants results from chemical reaction with the moving surfaces. Such lubrication is, in effect, a problem of controlled corrosion. The sulphur compounds investigated are (1) sulphides and disulphides which are inactive, (2) acidic bodies which form soaps—and are effective boundary lubricants, and (3) such bodies as the dithiocyanates. It is conceivable that "active" sulphur is set free and combines with the metallic surface under extreme conditions of temperature and pressure.

Molecular adsorption and surface states in lubrication are the topics of a paper by J. J. Trillat.<sup>79</sup> A general discussion is advanced on the influence of molecular structure on adsorption. Brief mention is made on the use of radioactive tracers in the study of adsorbed oil films.

There are a few papers concerned with the synthetic production of hydrocarbon lubricants. The production of olefin-polymer lubricating oil of satisfactory oxidation stability is dealt with by G. H. Dazeley, D. Gall, and C. C. Hall.<sup>80</sup> These authors describe attempts that have been made to increase the oxidation stability of Fischer-Tropsch oils

which fail to pass Air Ministry specifications, for example, by controlled hydrogenation, treatment with aluminium chloride and addition of naphthalene before polymerisation.

M. R. Dupas<sup>81</sup> reviews the chief methods for lubricating-oil syntheses and gives a description of the process in use at the Standard-Kuhlmann plant at Estaque. A Friedel-Craft condensation of benzene with dichloroethane and a chlorinated Fischer-Tropsch gas oil is accomplished. Transformer oil, light engine oil, and a bright stock of good quality are claimed.

### Reviews and surveys

Having regard to the manifold difficulties in printing and publishing during the war years and indeed for some prolonged period afterwards it is reasonable to expect that a number of reviews and surveys should be now appearing. Some of these are referred to in this section of the Report.

A symposium of German work in petroleum technology<sup>82</sup> during the war years is described by D. S. Petty, E. P. Wright, and F. H. Garner,<sup>83</sup> and deals with oxidation and combustion phenomena in general, including knock-prevention. The use of nitro-paraffins as engine fuels is discussed.

M. O'Farrell<sup>84</sup> describes work on the compression-ignition system.

E. D. Tingle<sup>85</sup> gives an outline of fundamental work on friction and lubrication and points out the over-riding need for synthetic products, a subject which is discussed by H. L. West<sup>86</sup> in considerable detail and from the point-of-view not only of war desiderata but also of industrial needs. The statement is made that "the Germans have based their petroleum products on the considerable structure of their chemical industry and, what is more, have been very successful and have achieved remarkable results."

The U.K. petroleum industry in war is the topic discussed by Sir Andrew Agnew (President of the Institute of Petroleum).<sup>87</sup> A striking picture of the work of the Petroleum Board during the war not only in defence but in attack is provided. The Petroleum Warfare Department worked on the design and perfection of flame throwers of many types, "the pipeline under the ocean"—Pluto—was a great achievement; F.I.D.O. for fog disposal was another successful effort. In effect, the whole industry was mobilised. England was turned into an immense oil dump. All the great Admiralty installations were "doubled up"—Portlake duplicated Newhaven, Hamble duplicated Portsmouth. The Petroleum Board prepared the large fleet of fuel-supply ships that made possible the great crossing of the Channel.

On the aviation side came a massive feat of organisation. Something of the order of a million tons a year of aviation spirit was forthcoming, and that, of course, of the highest octane rating.

The oil shale deposits of the world and recent developments in their exploration and utilisation reviewed up to May 1947 is a valuable summary prepared by W. H. Cadman<sup>88</sup> for the 7th International Congress of Pure and Applied Chemistry (London 1947). It affords a survey of the oil shale deposits in Great Britain, France, Estonia, Sweden, Spain, Portugal, Italy, Czechoslovakia, U.S.S.R., Canada, South Africa, Turkey, Bulgaria,

Germany, Japan, Australia, New Zealand, India, Burma, Brazil, and U.S.A.

R. C. Gunness<sup>89</sup> also reviews the world situation. The U.S. demand for petroleum products, which has quadrupled during the past 25 years, is expected to increase by a further 30% by 1970, when the total demand will be  $> 7 \times 10^6$  barrels per day. Residual fuel oil for use in industrial installations is a normal by-product of petroleum processing, but technological improvements, e.g., catalytic cracking, have enabled its production to be reduced progressively and this tendency will be reinforced by economic considerations. Improved petrol quality is to be anticipated, with cars using fuel having an octane number of 95, and also higher quality fuel for high-speed Diesel engines. Gas-turbines, with blades vulnerable to ash and corrosion, will require clean distillates. The greater demand for high octane motor spirit is offset by the greater use of compression-ignition engines and by the swing over to jet and turbo-jet power plant in aircraft.

C. V. Hill, H. T. Lorne, and A. R. Mercer,<sup>90</sup> in a report on motor gasoline from Middle East crude, point out that the straight run gasolines are characterised by relatively low octane number and generally high sulphur content but the middle distillates are of high grade quality. Sweetening and catalytic desulphurisation are applied, and upgrading processes such as thermal reforming and hydro-forming are utilised. Data are presented of yield-octane-number-T.E.L. relationships for sweetened, desulphurised Iranian straight-run gasolines and for the combined products of reforming and catalytic desulphurisation; of reforming and sweetening; of reforming and catalytic polymerisation and, finally, of hydroforming and of catalytic desulphurisation. Tests on numerous gasoline blends are given.

In a review of Middle East oil<sup>91</sup> up to date information, statistical, and economic, is given. Special articles by G. M. Lees on the Oilfield Province of the Middle East, political problems by M. W. Thonberg, the Middle East by C. Holme, and aerial surveying by T. D. Weatherhead, are included.

J. A. Oriol<sup>92</sup> deals with developments in technique in fuels and lubricants. Improvement in solvent extraction and cracking are reviewed. The most recent problem in the industry is production of fuel for gas turbines.

Hydrogenation (the Melchett Lecture, Institute of Fuel) is reviewed by K. Gordon.<sup>93</sup> This survey deals with the manufacture of hydrogen and carbon monoxide for the production of ammonia and methanol. A variety of catalytic processes is described leading to the production, *inter alia*, of higher alcohols, esters, amides, and acid anhydrides. The production of isooctane, butadiene, the hydrogenation of aromatic hydrocarbons, the dehydrogenation of naphthenes, the hydrogenation of phenols are indicated. A section of considerable interest deals with suitable catalysts.

F. H. Burstall, F. G. Lane, and J. B. Ditcham<sup>94</sup> provide a review of researches on the production of carbon black from tar products and petroleum residues by an impingement process. All the essential operating factors are considered together with tests of the finished material, with special reference to rubber reinforcement.

### Bibliography of petroleum literature

A specially hearty welcome should be given to the new *Institute of Petroleum Review*, the second volume of which is available. This publication is designed to give up-to-date surveys of oil matters, of meetings, lectures, and news in the industry—whilst the invaluable *Journal* of the Institute is reserved for the diffusion of research and for original communications.

To indicate the value of the *Review* mention may be made here of the following articles<sup>95</sup>: *March* 1948, "Vladimir N. Ipatiev—a Discourse in Honour of the Eightieth Birthday of a Very Famous Chemist and Oil Technologist"; *May* 1948, "The Significance of Anglo-American Co-operation in the Field of Oil Measurement Standardisation," by H. Hyams<sup>96</sup>; "Synthetic Detergents Derived from Petroleum Products," by P. L. Stedehonder,<sup>97</sup> P. W. O. Wijga,<sup>98</sup> and H. F. Dammars.<sup>99</sup>; *June et seq.* 1948, "James Young, Founder of the Mineral Oil Industry," by E. M. Bailey<sup>100</sup>; this is a contribution of outstanding merit. It is perhaps natural but none the less unfortunate that a new industry is careless of its pioneers. Mr. Bailey for so long a time chief chemist of Scottish Oils Ltd. and himself a notable pioneer, has performed a pious act in bringing forward the technical and scientific achievements of a great fellow-countryman. It is much to be hoped that the author will find the time to expand these notes into a monograph that will be of the greatest interest to all oil technologists. Another valuable survey in the *June* number is by J. A. Oriel<sup>101</sup> on "Petroleum in the Modern World." The author devotes special attention to the chemical derivatives of mineral oil but also discusses generally motor fuel, lubricants, the gas turbine, the Diesel engine and the economic use of fuel and power; in this connection he shows that in the year 1946 the sources of energy then available were (for 1920 the figures being 100).

Coal	107
Mineral oil	395
Hydro-electric	350, or in other words

	1920	1946
Coal declining from	88%	to 68%
Petroleum rising from	9.5%	to 26%
Hydro-electric rising from	2.5%	to 6%

*August*, 1948, "The Form of the Oil Industry," by D. E. Doyle.<sup>102</sup> The author comprehensively discusses the international integration of petroleum—production refining, transport, and distribution in the U.K., U.S.A., Russia, Mexico, Venezuela, and the Middle East. This number also contains an account of the visit of the A.S.T.M. delegates, L. C. Burroughs and I. G. Detwiler, to discuss co-operation in standardisation. In the *September* issue is an informative article by C. M. Cawley<sup>103</sup> on "Hydroforming," by C. G. Williams,<sup>104</sup> who surveys the engine performance of lubricants and in the *October* issue he affords a very useful insight into recent research and experience in this field; in the *December* number E. M. Bailey<sup>105</sup> continues his story of the life of James Young, with an historical outline of the dawn of petroleum refining in 1848,

pointing out that Young's basic methods of refining were in use for natural petroleum for many years after their original discovery.

*Modern Petroleum Technology*, Institute of Petroleum 1946, London, pp. 466. This exceedingly valuable summary of our present knowledge of the science and technology of mineral oil was issued not only to make available the knowledge of those expert in one field of the industry to those engaged in other branches, but also to fill the gap in publication caused by the war years. Broadly, it covers exploration, geophysics, production, chemistry of oil, refining, utilisation, and distribution. In no way is the treatment elementary.

*American Petroleum Refining*. H. S. Bell; London, Constable and Co. 1945, 3rd edition, gives an account of the newer refining processes which have come into use in the last few years. Distillation, fractionation, and heat transfer are considered in some detail. Cracking in general, thermal cracking, catalytic cracking (covering the Houdry process), thermofor and fluid catalytic cracking are all adequately treated. Chemical treatments, solvent extraction, and clay treatments are fully discussed.

*Synthetic process* [see also K. Gordon, J. Inst. Petrol. 1947, **33**, 469]. B. H. Weil and J. C. Lane [Remsen Press, Brooklyn, N.Y. 1948] have published the first systematic treatise devoted to the production of synthetic petroleum by the now numerous variants of the Fischer-Tropsch process. They deal *in extenso* with the production and purification of synthesis gas, and the products of the reaction. Originally, the Fischer-Tropsch gasoline was of low octane value, but the number has been pushed up to 80 in recent years so that the process has become an economic possibility even although at present it cannot compete with natural petroleum. With natural gas production at the present level, naturally the centre of interest is in America but, undoubtedly, the results of work now in progress will greatly influence commercial development in the rest of the world.

*Distillation and Rectification*. E. Kirschbaum, translated by M. Wulfinghoff, New York, Chemical Publishing Co. Inc. 1948, pp. 430. The original German edition was published in 1940, and is a valuable contribution to the literature.

Universal Oil Products Co. *Test Methods for Petroleum and its Products*, Chicago, U.O.P. Co. 1948. Special tests, supplementary to the A.S.T.M. handbook, are included.

*Natural Gasoline and the Volatile Hydrocarbons*. G. G. Brown, D. L. Katz, G. G. Overfell, and R. C. Alden 1948, Oklahoma, Natural Gasoline Association of America, pp. 92. This is a useful compendium dealing with vapour pressure, density, compressibility, and critical properties of the more volatile hydrocarbons.

*Selected Values of the Properties of Hydrocarbons*. F. D. Rossini *et al.*, U.S. Government Printing Office, Washington 1947, pp. 483: a collection of 385 tables comprises fundamental constants, conversion factors, selected values of properties together with specific and general references.

*Fuel and the Future*. London, H.M.S.O., 3 volumes, 1948: of interest to the petroleum chemist is the section in Vol. 2 containing useful articles

on liquid fuel for high-temperature processes by J. C. Bailey, F. J. Battershill, and R. J. Bressey, the use of oil in open hearth steel-furnaces by W. F. Cartwright, oil firing in the ferrous metal industry by A. Stirling, oil fuel for the non-ferrous metals by J. Sykes, oil for glass melting by E. J. C. Bowater and oil firing on the railways by A. W. J. Dymond. Improved fuel burning appliances are discussed by J. S. Jackson, indicating that bottled gas ( $C_3$  and  $C_4$  hydrocarbons) is steadily making headway, especially for domestic consumption in country districts, that over 2.5 million kerosine heaters are in use and over 1 million cookers, indicates that kerosine is an economical fuel and is making considerable headway and that wickless burners have been introduced and thermostatic devices have been perfected.

*Industrial Waste Disposal for Petroleum Refineries (and Allied Plants).* W. B. Hart, National Petroleum Publishing Co., Cleveland, U.S.A. 1947, pp. 103. This collection of articles that have appeared in *National Petroleum News* is concerned with the handling and disposal of liquid waste in which oil is present.

*Elements of Fuel Technology.* G. W. Himus, London, Leonard Hill Ltd. 1947, pp. 506. A useful introduction is provided for the student and the technologist, dealing with solid, liquid and gaseous fuels.

*Physical Constants of Hydrocarbons.* Vol. IV. Data concerning polynuclear aromatic hydrocarbons are very completely set out. G. Egloff, New York: Reinhold Publishing Corp. 1947, pp. 540.

*The Chemistry of High Polymers*, by C. E. H. Baum, Butterworth's Scientific Publications Ltd., London 1948, pp. 249. This monograph deals with the structure of high polymeric molecules and the problems of the condensation and addition polymers. Method of molecular weight and shape determination, fractionation and molecular weight distribution are discussed.

*The Chemistry of High Polymers and Surface Chemistry*, by H. W. Melville and E. K. Rideal, Heffer and Sons, Cambridge. Two sets of post-graduate lectures given before the Oil and Colour Chemists' Association are here gathered together. Of the highest authenticity they comprehend the latest views on the synthesis of high polymers, molecular size, molecular structure, reaction of solid surfaces, catalysis and reactions in monolayers.

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# FATS, FATTY OILS AND DETERGENTS

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**A**LTHOUGH little of outstanding novelty has appeared since the last report on this subject was made, the literature reflects a continued attack on the various problems of interest and industrial importance in the chemistry of fats and detergents. A large proportion of the work, much of it technical, is from American sources, but a number of Indian papers dealing with the fatty acid and glyceride structure of Indian seed oils should be noted. The results of the interesting investigations being carried out at the University of Capetown into South African fish products continue to reach us regularly, as also do the publications from our own University of Liverpool. There is an increasing interest in synthetic detergents and in methods of analysis, and it would appear that the complex subject of detergency is at last yielding to the prolonged efforts of scientific investigation.

No attempt will be made to present a detailed review of the literature. Discussion will be largely confined to those papers considered to be of general interest, particularly when definite advances have been made in our knowledge and understanding of the subject concerned.

## Oil seeds

It is not surprising that a correlation should exist between the germinating ability and the free fatty acid content of cottonseed, but it is nevertheless of interest that 93½% of those seeds containing 1–30% of fatty acid were found to be dead, whereas the proportion of dead seeds was only 4½% in the group containing less than 1% of fatty acid. All seeds containing more than 5% of fatty acids were dead.<sup>1</sup> It is obviously desirable that methods of detecting deterioration in stored seed should be available other than the development of free fatty acids and the failure of the seed to germinate. The appearance of the so-called red gossypol in cottonseed has now been shown to be an indication of deterioration, and an increase in the absorption of the extracted oil at 236 mμ. has also been noted as a result of prolonged storage of the seed. The same spectrophotometric changes have been observed also in peanuts stored at room temperatures for four years, but these phenomena have not yet been correlated with increase in the content of fatty acids. In neither seeds do these changes take place when they are stored at 1°.<sup>2</sup>

Protection of cottonseed from deterioration during storage has been shown to result from dielectric heating. The effect of a high frequency electric field (14 megacycles per second) was to remove moisture from the seed and to destroy the lipolytic enzymes responsible for fatty acid development. Temperatures above 100° were reached in less than 1 minute and treatment for 2 to 5 minutes was found to be effective in preventing the formation of fatty acids during storage at

38.5°. That the destruction of enzymes was the principal factor involved, was proved by the fact that seed containing 20% of moisture (the moisture content was increased to this figure after the seeds had been heated dielectrically) was found to be in good condition after storage. Untreated seed containing 20% of moisture developed 15½% free fatty acids when stored under the same conditions.<sup>3</sup> A moisture content of 13% is considered to be the safe limit for storage of cottonseed but the conditions of storage are probably more important. In this connection, the effect of storage at 25° in atmospheres of known relative humidity has been determined on the moisture content of whole cottonseed and of its component parts. Except at high humidities such as 93%, equilibrium was reached within 8 days. At a relative humidity of 73½%, the equilibrium moisture content of the seed was 11½% and this increased rapidly until it reached the value of 20% for a relative humidity of 92½%.

*Extraction.*—When cottonseed is extracted with ligroin solvents, the meal must be cooked in order to inactivate the gossypol which is present; recent literature has described several investigations into the use of alcoholic solvents as the extracting media. An account has been given of the use of 91% isopropyl alcohol in a continuous extraction process at about 70°. This solvent removes gossypol along with the oil, and the extracted meal was proved by feeding tests to be much superior to hydraulic meal. Evaporation of the miscella gave an impure dark-coloured oil, but it was found that a liquid-liquid extraction of the miscella to separate the oil from fatty acids, phospholipids and gossypol was possible.<sup>5</sup> The use of absolute or 95% ethanol for the continuous extraction of soyabean flakes has also been described. Flakes containing less than 3% moisture were used. The extraction was carried out at 78° and the oil was recovered from the extract by cooling to 20°. The alcoholic layer which separated contained no more than 5½% of oil and very little water, and it could be used again in the extraction of another batch of soya flakes. The small amount of alcohol present in the separated oil layer was removed by distillation and this was the only distillation involved, one lot of alcohol having been used 85 times. The theoretical energy requirements of the process were stated to be only three-quarters of those of the normal extraction with hexane. Alcohol was chosen as the preferred solvent after much experimental work with hexane, di- and tri-chloroethylenes, carbon tetrachloride, isopropyl alcohol and isobutyl alcohol, as it was found to produce the best quality oil and meal.<sup>6</sup>

The pigments of cotton seed are contained in heavily walled glands of high mechanical strength and the presence of these pigments in cotton seed meal renders it fit only for use as a cattle food. The possibility of removing these glands, so that they have no adverse effect either on the meal or on the oil, has been investigated and a process has been devised in which flaked cottonseed meats were violently agitated in a suitable solvent. The flakes were disintegrated, the pigment glands were continuously removed by flotation and 60–70% of the oil was extracted by the solvent. A mixture of perchlorethylene and commercial hexane was used of specific gravity 1.378. It was found that the meats must be disintegrated sufficiently to pass an 80-mesh sieve before complete separation from the pigment glands could be effected. The remaining

oil could be extracted from the meal by the usual methods, preferably with the solvent mixture so that the extract could be used as the solvent for the flotation stage of the process. The disintegration unit was exhaustively investigated from the points of view of power consumption, peripheral speeds, and so on. A pale yellow meal was obtained practically free from gossypol (0.006%) and the oil was successfully refined to a product of prime colour.<sup>7</sup>

### Selective extraction

The fractionation of oils and fats by extraction with suitable solvents is a matter which has received considerable attention in recent years. It results in the production of new types of fatty glycerides not available from natural sources and moreover such products can be prepared with standardised properties and characteristics. For example, soyabean oil has been separated into two components, one having drying properties approaching those of linseed oil while the other is suitable for edible purposes without further refining. A fraction of high iodine number (about 196) has been obtained from linseed oil having properties similar to those of perilla oil; sardine oil has yielded a fraction useful in varnish composition, and vitamin concentrations have been prepared from fish-liver oils. A detailed description has been given of the continuous extraction of vegetable oils with furfural, this solvent having been chosen after exhaustive tests. Lack of stability was its main fault, but this was successfully overcome by avoiding exposure to light and excessive heat and by the use of an inert atmosphere. The column was operated at 80–125° F., depending on the oil to be fractionated and 6–14 parts of furfural were used to 1 part of oil. An interface was maintained, with furfural falling in drops through the upper phase and oil rising in drops through the lower phase. Such a process is in some respects analogous to distillation and part of the less saturated fraction may be fed to the bottom of the column as reflux. The extract was passed through a second column in which the oil was removed from the furfural by extraction with naphtha, the furfural retaining the pigments, unsaponifiable matter and fatty acids which were recovered separately. With soyabean oil, a 60–70% fraction of high iodine number was obtained (about 150), the other fraction having an iodine number of about 110. The less saturated fraction has been hydrogenated to give shortenings of excellent colour and quality.<sup>8</sup> In an investigation into the solvent fractionation of fish oils, it has been shown that the antioxidants of the crude oils become concentrated in the extract fractions.<sup>9</sup>

The interesting observation has been made that when poppyseed oil is extracted by solvents (furfural, ethyl alcohol and acetone containing 3–5% of water are examples) the dissolved fraction has the lower iodine number, but no explanation has been offered for this surprising phenomenon.<sup>10</sup>

### Hydrogenation

It has been reported that when linseed oil is hydrogenated in a continuous process under pressure at temperatures up to 400° F., there is

practically no selectivity in hydrogenation of the linolenic acid, although marked selectivity is obtained between oleic acid and the less saturated acids. The oil was hydrogenated to an iodine number of about 120, in an effort to produce a good drying product with "non-yellowing" properties similar to those of soyabean oil. From this point of view the oils obtained in a batch hydrogenation process were superior and were in some instances better than soyabean oil. About 31% of the hydrogenated linolenic acid appeared in the product as the 9-15 linolenic acid.<sup>11</sup> Hydrogenation of tall oil at 90° for 2 hours under a pressure of 30 atmospheres in the presence of 3% of Raney nickel has been stated to yield a good coloured product suitable for soap manufacture.<sup>12</sup> Hydrogenation of shark liver oil with 0.25% nickel catalyst at 120° has been claimed to deodorise the oil in 30-45 minutes. The keeping quality of the oil was considerably improved and only 7% of the vitamin-A was lost.<sup>13</sup>

The possibility of utilising dissociated ammonia for hydrogenation of oils and fats has been investigated and it was shown that consumption of hydrogen was similar to that for hydrogen from other sources. The apparatus was equipped with a vent which allowed gas to escape from the chamber and thereby maintained a constant partial pressure of hydrogen. The rate of the reaction was slower than normal, but lard, as well as fatty acids, were hydrogenated to an iodine number lower than 5. The ammonia dissociator was said to be simple to operate and to lend itself to automatic control. The hydrogen-nitrogen mixture needed no purification and poisoning of the catalyst was not observed.<sup>14</sup>

### Fatty acids and glycerol

A description has been given of the Colgate-Emery process for the continuous splitting of fats. The counter current reaction between water and fat is carried out without a catalyst in a pressure tower at 260-725 lb. per sq. in. Glycerol-water of 13-18% concentration is obtained from high grade stock and it is easily purified. The fatty acids are free from the unsaponifiable matter introduced by a splitting agent, they are of better colour than Twitchell acids and may be used without distillation for soap manufacture. The process is economical, using only 1 lb. of high-pressure steam for every 5 lb. of fat split, and 98% reaction is obtained.<sup>15</sup> The Twitchell process has been followed analytically in a factory batch of 15,000 lb. of crude coconut oil. The reaction has been shown to proceed in stages, the first products being fatty acids and diglycerides without the liberation of glycerol. By the time the production of glycerol and of monoglycerides had commenced, the diglycerides had reached their highest concentration (19.5%). The concentration of diglycerides remained greater than that of the monoglycerides however until the latest stages of the hydrolysis. The concentration of monoglycerides was never greater than 7%. All three reactions occurred together, the rate of reaction becoming slower with time, until the process was terminated at the point when the fat was split to the extent of 92%.<sup>16</sup>

It has been shown that when groundnut oil and the methyl esters of its fatty acids are saponified under identical conditions with a 10% excess of soda lye (25° Bé) the esters are much the more rapidly saponified.

For example, at 80–100°, the esters were saponified in a few minutes whereas the oil required 5 hours.<sup>17</sup>

An investigation has been made into the equilibrium in ternary systems of oleic acid, stearic acid and acetone or commercial hexane at a series of temperatures from – 40° to 0°. The solubility of stearic acid in these solvents, especially in hexane, was considerably increased by the presence of oleic acid, and it was shown that purification of oleic acid from traces of stearic acid could be effected by crystallisation from acetone or hexane at – 30° or – 40°, the stearic acid remaining in the mother liquors.<sup>18</sup>

Separation of solid from liquid fatty acids by crystallisation is interfered with by the acids of shorter chain length. They increase the solubility of the higher saturated fatty acids which are then more difficult to separate from the unsaturated acids. It has been proposed to remove the short chain acids by distillation, after which the residual acids can be separated efficiently by crystallisation from a solvent. As an example, unsaturated fatty acids containing less than 1% of saturated acids were obtained from soyabean oil.<sup>19</sup> Poly-unsaturated acids can be removed from oleic acid by heating the mixture with alkali at 280–310° whereby the more unsaturated acids are decomposed to give acid soaps of saturated acids, which can then be removed by the usual methods.<sup>20</sup>

### Esterification and inter-esterification

In the esterification of palmitic, lauric, and oleic acids by methyl and ethyl alcohols at 18° in the presence of various catalysts, it has been pointed out that separation of the ester from the reaction mixture will promote the progress and extent of the reaction. Provided separation occurs, the reaction is also favoured by excess of alcohol and in these circumstances economical esterification should be possible without heating. Methyl alcohol is more effective than ethyl alcohol in such a process and complete esterification is obtained in a few hours at room temperatures. Esterification by ethyl alcohol rarely exceeded 90–95% even after 4 days.<sup>21</sup> Zinc fluoride has been suggested as a catalyst for the esterification of fatty acids with glycerol.<sup>22</sup>

The subject of interesterification of oils and fats is receiving considerable attention at the present time both in the journals and in the patent literature. In most instances, the fat is heated in an inert atmosphere to a high temperature (*e.g.*, 225°) in the presence of a catalyst such as stannous hydroxide, or sodium alkoxide, when rearrangement of the fatty acids in combination with the glycerol molecules occurs. The result of such a process is a glyceride structure corresponding to a random distribution of the fatty acids. The process is obviously capable of producing considerable differences in structure and properties, particularly when the original glyceride structure shows a marked divergence from random distribution. Oleoil, for example, having a melting point of 26.5° and containing no fully saturated glycerides has been changed to a fat of melting point 44.5° with a fully saturated glyceride content of 16%.<sup>23</sup> On the other hand, a fat altered by interesterification will contain a lower proportion of trisaturated glycerides if it initially contained more than is required by random distribution of the fatty acids.

A patented process has suggested the molecular rearrangement of a

fat using sodium methoxide as catalyst, the product then being crystallised from solvents so that three fractions are obtained. The hard and the soft fractions are then returned to a batch of untreated fat. The intermediate fraction will be of sharply defined glyceride composition and it is claimed that a fat resembling cocoa butter can be prepared in this way from cottonseed stearin and hydrogenated soyabean oil.<sup>24</sup>

An interesting modification of these processes of molecular rearrangement has been termed directed interesterification and its object is to promote the maximum formation of trisaturated glycerides. The normal process of interesterification takes place in fats that are completely molten and the rearrangement of the fatty acids proceeds towards a random distribution but this equilibrium condition will not be attained if the process is effected at such a low temperature that the trisaturated glycerides crystallise from the mixture during the course of the reaction. This modified process is carried out in an inert atmosphere and in the complete absence of moisture, using sodium or potassium alkoxides as catalysts. After 16 hours at 70° F., with 0.2% sodium methoxide as catalyst, the cloud-point of cottonseed oil was increased from 26° F. to 82° F., whereas random inter-esterification at 120° F., raised the cloud-point only to 58° F. The directing effect of crystallisation is greater at lower temperatures but the speed of the reaction is reduced. It is possible therefore to commence the reaction at one temperature (with or without crystal seeding) and then progressively to reduce the temperature, finally holding the reaction products at room temperature for several days. In this way, as much as 19% of fully saturated glycerides were induced to form in cottonseed oil. An oil such as cottonseed can be converted to a semi-solid fat suitable for shortening and it is important to note, from the nutritional point of view, that the fat still contains its original unsaturated acids.<sup>25</sup> The method is obviously capable of a variety of modifications and applications. As an example, in a process for the manufacture of saturated mono- and diglycerides, palm oil is partially esterified with glycerol at 170°, and the resulting mixture is then treated at 100–105° F. with 0.2% sodium methoxide in xylene. The product rearranges to give a yield of 36% solid glycerides with a hydroxyl value of 242 and 72% of liquid glycerides having a hydroxyl value of 75.<sup>26</sup>

### Oxidative rancidity and flavour reversion

The fact that addition of oxygen to unsaturated compounds results in the formation of a hydroperoxide group attached to a carbon atom in the  $\alpha$ -position to a double bond has led to the formulation of two hypotheses. The first of these suggests that oxidation initially occurs at an ethylenic carbon atom and that the double bond then shifts to leave the (OOH) group in the  $\alpha$ -position: the second hypothesis asserts that addition takes place directly to an activated carbon atom in the  $\alpha$ -position and that because of resonance of the double bond, four isomeric hydroperoxides are possible. Only two isomers are possible according to the first theory.

In view of the analogy that exists between the reactions of oxygen and of maleic anhydride with unsaturated compounds, the nature of

the addition products of maleic anhydride with alkylbenzenes has been investigated. Substituted succinic acids were obtained by addition of one molecule of maleic anhydride to one molecule of an alkylbenzene containing a primary or a secondary alkyl group, but *tert*.-butylbenzene failed to react. The reaction occurred most readily with ethylbenzene and, in addition to benzylsuccinic acid, 2 : 3-diphenylbutane was formed during the reaction, a fact suggesting that the addition had taken place through a reaction involving the free phenylethyl radicle. The work proves that the reaction occurs through displacement of a hydrogen atom attached to a carbon atom in an  $\alpha$ -position to the double bond and affords presumptive evidence that peroxidation takes place in a similar manner, namely, by a free radicle mechanism initiated by the abstraction of hydrogen from the  $\alpha$ -carbon atom. The preparation and characterisation of the addition product of maleic anhydride with methyl oleate were then undertaken. One molecule of methyl oleate was shown to react with one molecule of maleic anhydride, giving a product in which the double bond had not been saturated. Among the products of oxidation of this compound, nonoic, octoic, suberic, and azelaic acids were identified, indicating the presence of four isomers in which maleic anhydride had been attached to carbon atoms 8, 9, 10, and 11 in the oleic acid chain. It was suggested therefore that the mechanism of the reaction involves addition to the  $\alpha$ -carbon atom in a resonating system and that considering the similarity between the reactions of maleic anhydride and of oxygen with unsaturated compounds, autoxidation of the double bond in methyl oleate may be a similar free radicle chain mechanism.<sup>27</sup>

The chromatographic separation of the autoxidation products of methyl linoleate has been attempted, using a sodium aluminium silicate as the adsorbent, the oxidised fractions being extracted after dividing the column into sections. A fraction with a peroxide value as high as 4000 m.e./kg. was obtained from an oxidised ester of which the peroxide value was 377 m.e./kg. Absorption at 231.5  $m\mu$ . and 275  $m\mu$ . was present in all the fractions to varying extents and was considered to be due respectively to the presence of the initial hydroperoxide product and to conjugated dienones.<sup>28</sup> It is of interest to note that the thermal decomposition products of the hydroperoxide of methyl oleate have been shown to contain 2-undecenal and that qualitative evidence suggested the presence of other similar unsaturated aldehydic substances.<sup>29</sup>

The stability of vegetable oils has been shown to increase rapidly to a maximum during the deodorisation process and then to fall somewhat to a roughly constant value, which was greater than that of the oil before deodorisation. In laboratory tests a similar improvement was obtained by the use of nitrogen instead of steam and also by simply heating the oil in a vacuum. It was concluded from these experiments therefore that thermal decomposition of pro-oxidant substances was the reason for the increased stability.<sup>30</sup> The marked improvement in the stability of oils caused by hydrogenation has been correlated by statistical analysis with the fatty acid composition of the hydrogenated products. This increased stability was proportional to the decrease in the oleic acid concentration after linoleic acid had been completely hydrogenated : while linolenic acid was present, the reciprocal of the induction period

was proportional to the linolenic acid content.<sup>31</sup> A study has been made of the antioxidant properties of gallic acid esters of some of the higher fatty alcohols. They were found to be much more soluble in fats than gallic acid or its lower esters and the antioxidant effect was carried over into baked pie crust much more than is the case with gallic acid or propyl gallate.<sup>32</sup> This property of "carry over" would therefore appear to be dependent on the solubility of the antioxidant in the fat, and it has been suggested that the ability of antioxidants to stabilise the baked product can be measured in the laboratory by determining the extent to which they are retained when the fat is extracted with an equal volume of hot water. A good correlation was found between these results and the "carry over" effect and it was found that the best antioxidants, from this point of view, were retained to the extent of 80–90% in the extraction test.<sup>33</sup>

Norconidendrin has been suggested as a new antioxidant for oils and fats, its activity being comparable with that of nordihydroguaiaretic acid. It has been prepared by demethylation of conidendrin, which can be extracted from the sulphite waste liquors produced during the pulping of western hemlock.<sup>34</sup> Butylated hydroxyanisole has been suggested as an antioxidant, especially for lard,<sup>35</sup> and hydrocaffeic acid and its alkyl esters have also been suggested as antioxidants.<sup>36</sup> The preparation of tocopherol from the deodoriser scum obtained from vegetable or animal oils can be facilitated by hydrogenating the scum and crystallising the product from acetone at  $-50^{\circ}$ . The tocopherol is concentrated in the solution and substances interfering with its isolation are removed.<sup>37</sup>

The question of flavour reversion in hydrogenated soyabean and linseed oils, and in soyabean oil itself, still constitutes an important problem for investigation. Several theories have been advanced to account for this phenomenon: lecithin has been held to be responsible, *isolinoleic* acid has been regarded as the precursor of the flavour in hydrogenated products, and it has been suggested that the precursor is contained in the unsaponifiable matter. Hydrogenated perilla oil, which contains a large amount of *isolinoleic* acid, has been shown to suffer flavour reversion when heated at  $200^{\circ}$ , but the odour was not obtained with hydrogenated tung oil. A concentrate of *isolinoleic* acid free from unsaponifiable matter gave the same odour when heated as did fatty acid fractions of hydrogenated linseed oil after they had been re-esterified with glycerol. The fractions containing most *isolinoleic* acid gave the most reverted odour.<sup>38</sup> Reversion has been shown to occur without significant increase in peroxide values or Kreis test intensities, and samples stored *in vacuo* in the dark do not develop flavour reversion. The susceptibility of fats of low iodine value suggests however that *isolinoleic* acid cannot be the only factor involved.<sup>39</sup> It has been noted that hydrogenated soyabean oils low in unsaponifiable matter show relatively greater stability. When the unsaponifiable fraction from partly hydrogenated soyabean oil was added to a refined arachis or cottonseed oil, even after careful deodorisation they developed a reverted flavour on storage. Addition of unsaponifiable matter from unhydrogenated refined linseed oil did not have this effect. By selective adsorption of a ligroin solution of hydrogenated soyabean

oil, the flavour stability of the fat was greatly improved though the content of polyunsaturated acids had not been changed. A similar result could not however be obtained with unhydrogenated soyabean oil.<sup>40</sup> German oil refiners consider that lecithin is responsible for flavour reversion and have maintained that this defect can be minimised by additional water-washing of the extracted oil and by the addition of 0.01% of citric acid during deodorisation. Flavour stability in soyabean oil has been shown to be much improved by this process, the keeping period of a treated oil being five times as great as that of a control. The conclusion reached however was that the treatment only delayed the onset of flavour reversion.<sup>41</sup> The off-flavour in both reverted hardened and unhardened soyabean oils has been shown to be present in the ether extract of the steam distillate. By vacuum distillation at room temperature a product was obtained which reacted with semicarbazide and with Girard's reagent-T to give compounds from which the original flavour could be regenerated. Two 2:4-dinitrophenylhydrazones were isolated and purified and the conclusion reached was that  $\alpha$ -heptenal was the carbonyl substance responsible. Its 2:4-dinitrophenylhydrazone had practically the same melting point as that of the compound prepared from unhydrogenated soyabean oil and the two compounds gave identical X-ray diffraction patterns. The dinitrophenylhydrazone prepared from hydrogenated soyabean oil was apparently different. It had a slightly lower melting point and gave a long spacing value of 17.8 Å, whereas the  $\alpha$ -heptenal compound and the compound from soyabean oil gave a value of 17.1 Å.  $\alpha$ -Heptenal added to soyabean oil did not, however, produce the characteristic reverted flavour.<sup>42</sup>

### Glyceride and fatty acid composition of various oils and fats

The seed oils from three West African citrus fruits (grape fruits, sweet oranges and limes) have been found to have a fatty acid composition and glyceride structure showing considerable resemblance to cottonseed oil, particularly in the relatively high proportion of palmito-glycerides. The main difference was the presence in these oils of small amounts of linolenic acid. The fatty acid compositions are given in Table II and the glyceride structures deduced for two of the oils are :

	Tri-saturated	Di-saturated	Mono-saturated	Tri-unsaturated
Sweet orange ..	—	27%	50%	23%
Lime .. ..	2%	25%	55%	18%

The grape fruit oil was hydrogenated to an iodine number of about 70 and a soft white fat, suitable for use as a lard substitute, was obtained. All three oils were considered suitable for edible purposes.<sup>43</sup>

An examination of the glyceride composition of soyabean oil has shown that the fatty acids are evenly distributed so that about 70% of the glyceride molecules contain two polyunsaturated acids and only about 5% contain three. The linolenic radicles are distributed singly, in about 25% of the oil. Crystallisation of the oil from acetone at  $-40^{\circ}$  gave a soluble fraction of about 37% and linolenic acid occurred singly in about 40% of the glycerides in this fraction. Over 30% still contained

one saturated acid radicle and it is apparent that such a fraction cannot be an efficient drying oil.<sup>44</sup>

The fatty acid composition of some Indian seed oils is presented in Table II and in the following instances the glyceride composition was also given.

	Radish <sup>45</sup>	Wild safflower <sup>46</sup>	Sunflower <sup>47</sup>
Mono-saturated .. .. .	36	23	31
Oleo-dilinolein .. .. .	—	11	24
Di-oleo-linolein .. .. .	—	62	45
Eruco-di-unsaturated .. .. .	26	—	—
Tri-unsaturated, mostly triolein ..	38	3	—

Neat's foot oil has been examined and found to contain probably less than 10% of triolein. The conclusion was reached that the lubricating properties of this oil probably result from the presence of about 23% of hexadeceno-diolein (and possibly also from the dioleo-glycerides in which the third acid radicle is a polyethenoid C<sub>18</sub>, C<sub>20</sub>, or C<sub>22</sub> acid) and not from triolein as has been generally supposed. The fatty acid composition of the oil is given in Table I: the component glycerides were disaturated glycerides 7%, mono-saturated 54% (containing 35% of palmito-diolein), tri-unsaturated 39% (containing 23% of hexadeceno-diolein and 8% of polyethenoid-diolein).<sup>48</sup>

A series of papers on South African fish products has been concerned with the liver oils of four species of shark, and the fatty acid composition of the glyceride portion of these oils is given in Table I. In the case of the Soupfin shark (*Galeorhinus canis*) the liver oils from fat and gravid female fish, from the foetus and also from the male fish were examined separately, and the original paper should be consulted for further information on this aspect of the subject. In fact, such a large amount of data of great interest has been presented in these three papers that it cannot be adequately summarised here. The unsaponifiable portions of the oils were exhaustively analysed and the following table gives a summary of the outstanding features.

	% Unsaponifiable matter in liver oil	Composition of unsaponifiable matter
Basking shark .. .. .	30-50	Mainly hydrocarbons (chiefly squalene).
Spiny shark .. .. .	About 50	Mainly squalene, with some $\alpha$ -glyceryl ethers
Seven-gilled shark ( <i>Heptranchias pectorosus</i> )	About 20	Mainly $\alpha$ -glyceryl ethers with some sterols
Soupfin shark ( <i>Galeorhinus canis</i> ) .. .. .	Up to 10	Vitamin-A, $\alpha$ -glyceryl ethers, sterols and fatty alcohols

The vitamin-A content of the first three oils was negligible and in the case of the soupfin shark very little vitamin-A was found in the foetus liver oil, which contained a high proportion of cholesterol.<sup>49</sup> The unsaponifiable matter of dogfish liver oil has been examined qualitatively, cholesterol, vitamin-A, selachyl, and chimyl alcohols being identified.<sup>50</sup>

The fatty acid and glyceride composition of an Antarctic whale oil (which had been examined previously) have been reinvestigated by

Table I  
FATTY ACID COMPOSITION AND ANALYTICAL CONSTANTS OF SOME ANIMAL OILS

	Neat's foot oil <sup>a</sup>	Shark liver oils <sup>a</sup>					Grey seal blubber <sup>a</sup>	Turtle oils (d) <sup>a</sup>					Tiger fat <sup>a</sup>
		Basking shark	Spiny shark	Seven-gilled shark	Soupin shark (b)	Soupin shark (c)		<i>Dermatemyx nasuti</i>	<i>Chelone mydas</i> (summer)	<i>Chelone mydas</i> (winter)	<i>Caretta caretta</i>	<i>Lepidochelys olivacea</i>	
Saturated acids	—	—	—	—	—	—	—	10.2	—	—	—	—	
Lauric ..	—	—	—	—	—	—	—	9.4	8.2	6.6	1.8	1.3	
Myristic ..	0.7	2.1	3.9	1.6	3.3	3.3	3.7	17.2	16.7	21.8	26.1	11.8	
Palmitic ..	16.9	13.6	20.4	16.6	17.7	18.5	10.5	7.0	5.6	15.5	5.5	26.8	
Stearic ..	2.7	3.2	6.9	6.9	1.6	2.2	2.0	1.4	3.5	1.9	—	6.0	
Arachidic ..	0.1	3.6	0.3	1.3	0.7	0.5	—	—	—	—	—	—	
Behenic ..	—	3.2	0.2	1.6	—	0.1	—	—	—	—	—	—	
Unsaturated acids													
C <sub>18</sub> ..	1.3 (-2.0)	0.5 (-2.0)	1.6 (-2.0)	0.7 (-2.0)	.5 (-2.0)	0.7 (-2.0)	1.6 (-2.0)	0.9 (-2.0)	4.4 (-2.0)	3.5 (-2.0)	—	—	
C <sub>18</sub> ..	9.4 (-2.0)	11.9 (-2.0)	11.9 (-2.0)	11.0 (-2.0)	9.4 (-3.1)	6.3 (-2.0)	15.5 (-2.2)	9.9 (-2.0)	13.6 (-2.0)	18.0 (-2.0)	11.7 (-2.0)	—	
C <sub>18</sub> ..	(a) 64.4 (-2.0)	12.8 (-2.3)	25.6 (-3.0)	30.3 (-2.5)	25.3 (-3.7)	17.5 (-3.4)	30.8 (-2.7)	32.4 (-2.6)	38.0 (-3.1)	31.4 (-3.7)	40.1 (-3.1)	53.9 (-2.0)	
C <sub>18</sub> ..	1.6	23.2 (-4.0)	15.4 (-6.6)	15.6 (-5.4)	21.4 (-8.0)	20.9 (-8.3)	16.5 (-5.7)	10.8 (-8.2)	10.0 (-6.5)	1.3 (-8.6)	14.8 (-5.0)	—	
C <sub>22</sub> ..		20.0 (-3.6)	13.9 (-8.1)	13.0 (-8.7)	15.9 (-10.3)	25.5 (-10.6)	18.1 (-10.6)	—	—	—	—	—	
C <sub>24</sub> ..		5.6 (-5.9)	—	—	1.4 (-10.0)	1.2 (-10.0)	4.6 (-10.0)	—	—	—	—	—	
Unresaponifiable matter (%)	0.3	47.7	48.5	19.6	2.52	8.68	0.5	0.84	2.2	3.0	1.86	0.74	
Density	1.4610(40)	—	—	—	—	—	—	0.9650(30)	—	0.9281(20)	0.9301(20)	0.9122(30)	
Refractometric index		—	—	—	—	—	—	1.4580(40)	—	1.4634(40)	1.4639(40)	—	
Saponification value		—	—	159.5	186.0	169.7	180.4	183.0	198.4	183.5	189.0	181.6	
Iodine value	73.3	208.7	244.4	118.9	196.0	215.6	162.2	73.5	89.2	76.6	93.3	56.8	

(a) Plus 2.3 (-4.0) and 0.7 (-6.0).

(b) Female fish in non-gravid condition.

(c) Foetus.

(d) Optical activity was not found in any of these oils. *Derma. mairii* is a fresh-water turtle.

Table II  
FATTY ACID COMPOSITION AND ANALYTICAL CONSTANTS OF SOME VEGETABLE SEED OILS

	% oil	Density	Refractive index	Saponi- fication value	Iodine value	Unsaponi- fiable matter %	Palmitic	Stearic	Oleic	Linoleic	Linolenic
<i>Amaranthus polygamus</i> <sup>24</sup>	4.3	0.9109 (25)	1.4693 (—)	182.2	100.6	1.89	—	—	34.2	43.6	—
<i>Anacardium occidentale</i> <sup>25</sup>	—	0.9142 (15)	1.4687 (—)	176.5	98.0	2.18	—	—	—	—	—
<i>Bacca oaxana</i> (Cajuparilaceae) (Sudan) <sup>26</sup>	—	—	—	175.2	—	9.96	—	—	31.4	26.8	—
<i>Batis fruticosa</i>	19	0.9076 (30)	1.4791 (30)	184.8	85.1	1.89	19.4	8.3	25.5	23.5	—
<i>Calda triagifolia</i> (Ulmaceae) (Sudan) <sup>26</sup>	—	—	—	187.1	—	2.09	—	13.6	13.7	73.7	—
<i>Chenopodium muricarpa</i> (Ulmaceae) (Sudan) <sup>26</sup>	—	—	—	189.7	—	2.88	—	12.4	9.6	82.0	—
<i>Chenopodium pitcaud</i> (Euphorbiaceae) (Sudan) <sup>26</sup>	—	—	—	185.2	—	0.70	—	—	21.1	48.9	—
<i>Citrus fruits</i>	41	—	1.4706 (25)	195.5	100.8	0.3	27.5	2.9	21.1	39.3	5.9
{ Grape fruit (Marsh) <sup>26</sup>	43	—	1.4687 (25)	197.2	100.2	0.3	28.9	2.1	25.1	36.6	5.9
{ Sweet Orange <sup>26</sup>	40	—	1.4686 (25)	195.3	97.6	0.6	23.8	8.3	24.8	37.1	6.3
{ (West Indian)	39	—	1.4676 (25)	195.2	111.1	0.6	36.1	9.6	11.1	39.3	13.1
<i>Colliguaya interperima</i> <sup>27</sup>	52	—	—	—	—	—	10.0	—	30.2	31.5	30.1
{ <i>Argyria spectiosa</i> <sup>28</sup>	31.2	0.9377 (23)	—	189.1	123.1	1.38	—	—	25.6	50.8	9.2
{ <i>Argyria spectiosa</i> <sup>28</sup>	10.7	0.9351 (30)	1.4554 (30)	187.5	76.0	0.3	10.1	1.9	33.2	13.2	6.1 (b)
{ <i>Ipomoea batatas</i> <sup>28</sup>	9.4	0.9180 (20)	1.4740 (20)	180.5	121.5	1.98	6.7	29.1	44.0	14.5	6.0 (c)
{ <i>Ipomoea batatas</i> <sup>28</sup>	8.7	0.9164 (30)	1.4529 (30)	200.0	68.6	—	5.9	20.4	41.0	15.2	3.9 (d)
<i>Grevia villosa</i> (Ulmaceae) (Sudan) <sup>26</sup>	30.8	0.9175 (30)	1.4790 (30)	184.6	131.0	3.40	13.6	15.9	42.3	41.8	—
Gourd (perennial) <i>Cucurbita palmaria</i> <sup>28</sup>	—	—	—	180.8	122.7	1.2	—	—	30.4	43.0	—
Hedge mustard, <i>Sisymbrium irio</i> <sup>28</sup>	28.1	0.9134 (30)	1.4762 (30)	191.3	109.4	1.1	8.1	3.0	37.2	34.7	—
<i>Hibiscus</i>	18-20	0.9083 (30)	1.4672 (30)	176.3	121.3	1.33	23.0	5.0	43.3	22.0	—
<i>Letitica leucostoma</i> <sup>29</sup>	14.5	0.9183 (30)	1.4704 (30)	194.4	121.3	2.2	4.0	3.7	37.0	47.0	—
<i>Leptanion scirpoides</i> <sup>29</sup>	—	—	1.4580 (21)	181.4	0.95	0.95	7.1	13.2	37.4	15.3	—
<i>Putranjiva, ramburghii</i> <sup>29</sup>	41.8	0.9070 (21)	1.4750 (30)	187.1	103.1	0.84	1.3	1.4	60.4	4.5	3.6 (a)
<i>Radiata, R. holosericea</i> <sup>29</sup>	—	0.9075 (30)	1.4704 (30)	178.5	102.3	0.9	2.0	5.5 (i)	12.5	13.6	8.5 (g)
<i>Rape seed, Indian</i> <sup>29</sup>	—	—	—	174.3	84.2	0.7	2.0	7.5 (i)	16.5	16	7.0 (g)
{ <i>Argemone</i> <sup>29</sup>	—	—	—	176.1	104.0	0.7	2.5	4.0 (i)	14	12	7.5 (g)
{ <i>Polish</i> <sup>29</sup>	—	—	—	171.6	90.9	1.3	3.0	3.5 (i)	15.5	21	10.0 (g)
{ <i>Ravison (Black Sea)</i> <sup>29</sup>	—	—	—	171.6	18.6	0.8	4.0	5.0 (i)	24	9	6.5 (g)
<i>Jamba (Indian)</i> <sup>29</sup>	—	—	—	182.9	145.3	1.1	3.1	3.6	55.8	36.8	—
<i>Safflower (wild) Carthamus oxyrrhiza</i> <sup>28</sup>	—	0.9175 (35)	1.4715 (30)	182.9	112.3	0.42	2.1	2.6	48.4	40.5	—
<i>Sunflower, Helianthus annuus</i> <sup>28</sup>	52.5	0.9147 (25)	1.4732 (25)	184.7	111.6	0.55	3.3	3.6	56.0	16.1	—
<i>Svedenia makoyana</i> <sup>29</sup>	—	0.9179 (27)	1.4720 (25)	201	118-139	1.8	9.5	13.4	23.7	53.0	—
<i>Tobacco, Nicotiana glauca</i> <sup>29</sup>	—	0.9230 (15)	—	191.4	—	—	17.1	6.2	25.5	56.8	—
<i>Trema guineensis</i> (Ulmaceae) (Sudan) <sup>26</sup>	—	—	—	180.7	88.6	0.95	27.9	—	23.7	39.7	—
<i>Ficus religiosa</i> (Ulmaceae) (Sudan) <sup>26</sup>	—	—	—	188.0	—	1.11	2.3	22.6	61.1	24.0	—
<i>Ficus religiosa</i> (Ulmaceae) (Sudan) <sup>26</sup>	38.5	0.9315 (25)	1.4780 (36)	—	—	—	—	—	—	—	—

(a) Arachidic 5.5, Behenic 5.2.

(b) Behenic 6.6

(c) Arachidic 7.8.

(d) Behenic 3.8.

(e) 12% and 10% respectively conjugated trioleic

acid, not identical with  $\alpha$ - or  $\beta$ -elaeostearic.

(f) Erucic 17.2

(g) Phenyl isocyanate 0.7

(h) Erucic 22.0, Arachidic 3.0, Behenic 3.4.

(i) C<sub>17</sub>-C<sub>18</sub> saturated acids.

(j) Erucic, 47.5, 47.5, 52.6, 45, 39, 37.5 respectively.

(k) Hexadecenoic, 1.5, 0.5, 3, 2.5, 0.6, 1.5 respectively.

(l) Eicosenoic, 5, 6, 3.5, 5, 4, 11.5 respectively.

(m) Saturated acids not separable cf. daturic.

improved methods. The acids were fractionated by crystallisation from solvents at low temperatures and the results of the analysis agreed well with those obtained previously by preliminary separation of the lithium and lead salts. Owing to better separation of the glyceride fractions however a more accurate picture of the glyceride composition of the oil was obtained. 2.5% tri-saturated glycerides, 16% di-saturated, 50% mono-saturated, and 30% tri-unsaturated glycerides were considered to be present. Oleic acid was a constituent radicle in over 90% of the glycerides.<sup>51</sup> By similar methods the oil obtained from a grey Atlantic seal (*Halichoerus grypus*) has been analysed. The liver contained less than 3% of fatty matter, which consisted of 50% glycerides, 29% phosphatides, and 21% unsaponifiable matter. The liver glycerides were more saturated than the blubber oil, the fatty acid and glyceride composition of which were determined. The glyceride structure was of the mixed type resulting from even distribution of the fatty acids, most of which occurred only once in any molecule. The probable components were di-saturated glycerides 6%, mono-saturated 45% (about 15% was monosaturated-dipolyethenoid) and tri-unsaturated glycerides 49%. The fatty acid composition of the oil is given in Table I.<sup>52</sup>

The component acids of yeast fat have been reported as the following: myristic 0.1, palmitic 25.6, stearic 5.9, arachidic and higher acids 5.1, hexadecenoic 1.3, oleic 54.5, octadecadienoic 5.7, octadecatrienoic 0.7, C<sub>20-22</sub> enoic 1.1. The fat contained 2.4% of unsaponifiable matter and 33% free fatty acids.<sup>53</sup>

The fatty acid compositions of a number of oils and fats have been reported and the results are presented in Tables I and II. In both tables, minor amounts (less than 2.5%) of constituent acids have been omitted when they cannot be conveniently included in the tables and the original papers should be consulted for these further details. The temperature of determination is given in brackets after the figures for density and refractive index. In Table I, the degree of unsaturation is given in brackets after the percentage amounts of the acids: for example (— 2.0), signifies a mono-unsaturated acid.

### Drying oils

The fractionation of heat polymerised linseed and soyabean oils has been effected by successively extracting the product with the homologous series of normal alcohols. *n*-Propyl alcohol dissolved the fatty acids and the unpolymerised oil but none of the polymers; *n*-butyl alcohol dissolved the dimers but not the higher polymers, and so on. *n*-Lauryl alcohol was the highest alcohol to be used and it dissolved all polymers up to the hexamers. Beyond this point, ligroin was a satisfactory solvent for all the subsequent stages of polymerisation up to that of gelation, when the insolubility of the infusible, cross-linked polymers in this solvent afforded a method for their effective separation. There was a certain amount of overlapping in the above fractionation procedure, but the exact nature of the fractions obtained was calculated from the average molecular weights, which were determined cryoscopically using cyclohexane as the solvent. Viscosity and iodine values were determined on the fractions and the results provided a picture of the progress and

nature of the polymerisation process. Successive formation of higher polymers was clearly indicated at all stages, and evidence was obtained that the polymerisation of glyceride molecules involves two double bonds when linolenic acid is the radicle concerned, and one double bond in the case of linoleic and oleic acids. In this work the polymerisation was carried out at 307° and gelation was reached after 11 hours for linseed oil and 18 hours for soyabean oil, when the contents of insoluble cross-linked polymers were 30% and 17% respectively.<sup>73</sup>

The use of polymerisation catalysts has been studied and it has been shown that polymers produced by the heat bodying of linseed oil, using diphenyl sulphide as a catalyst, are inferior in performance to polymers obtained without a catalyst from conjugated oil.<sup>74</sup> Anthraquinone and its derivatives have been proved to be effective as polymerisation catalysts because they promote conjugation in the oil prior to polymerisation. The catalyst was recovered unchanged. No conjugation was obtained in similar experiments with other catalysts, for example, diphenyl sulphide, and it would appear therefore that more than one mechanism is involved in the heat bodying of vegetable oils.<sup>75</sup>

### Analysis of oils and fats

The suggestion was made several years ago that di-saturated glycerides could be determined, after oxidation of an oil or fat with potassium permanganate in acetone, by dissolving the acidic products of oxidation in ether and extracting the monoazela-glycerides (derived from the original di-saturated glycerides) with potassium bicarbonate solution. Part of the diazela-glycerides is also extracted, but determination of the saponification value enables a correction to be made. This method of analysis has now been proved to yield satisfactory results when applied to a known mixture of synthetic glycerides containing approximately equal amounts of tristearin, oleo-distearin, stearo-diolein, and triolein. The method would appear to be of limited application but nevertheless it should obviously be of value when information is available as to the nature of the glycerides concerned.<sup>76</sup> The oxidation of fat with potassium permanganate in acetone is also the basis of a method which has been proposed for the determination of linoleic acid. The azelaic glycerides are titrated with 0.1-N alkali, after removal by steam distillation of the volatile acids formed during the oxidation. One equivalent of alkali is used for every molecule of unsaturated acid in the original fat and the titration is, in effect, a determination of the unsaturated acids. The figure so obtained was used in conjunction with the iodine value for the determination of the oleic and linoleic acid contents of oils and fats, and the results agreed reasonably well with those obtained by other methods. Alternatively, if it be assumed that only  $C_{18}$  unsaturated acids are present the titration may be used to calculate the total unsaturated acids.<sup>77</sup> In the spectrophotometric determination of linoleic acid, it has been shown that a small absorption at 268 m $\mu$ . is not a reliable indication of the presence of this acid unless confirmation is obtained by another method such as the isolation of hexabromostearic acid.<sup>78</sup>

Two interesting papers have appeared on the separation and determination of fatty acids by partition chromatography. For the separation

of the lower acids, with from 5 to 10 carbon atoms, methyl alcohol was used as the stationary solvent on a column of silica gel, bromocresol green being used as an indicator. The fatty acids were added in *isooctane* solution and eluted in bands from the column with the same solvent. The volume of solvent required to wash a band to the bottom of the column (the threshold volume) afforded a ready means of identifying the fatty acid. This tentative identification was confirmed by rechromatographing the acid in admixture with a pure specimen, when the two should pass down the column as a single band. The higher acids moved through the column very quickly and did not interfere with the process. The acids lower than  $C_5$  were very strongly adsorbed at the top of the column. In normal separations a small amount of overlapping of the bands occurred and the accuracy of the determination was considerably improved by passing the fractions through a second column. In similar work with  $C_{11}$  to  $C_{19}$  acids, a mixture of furfuryl alcohol and 2-aminopyridine was used on the silica gel column with *n*-hexane as the eluting solvent. The percolate was collected in fractions which were titrated with standard sodium ethylate. In these conditions an indicator could not be used and the threshold volumes, as the acids were successively washed from the column, were used for tentative identification. Saturated fatty acids with an even number of carbon atoms were readily separated from each other as also were the odd-numbered acids, but mixtures of the two series could not be completely separated. It was necessary to remove unsaturated acids before the method could be applied. Such a procedure can obviously be used for the removal of impurities from fatty acids, and as little as 0.5% stearic acid in palmitic acid was separated and determined by working with large samples and refractionating the separated portions.<sup>79</sup>

A modification of the Wijs method for the determination of iodine values has been suggested which takes advantage of the catalytic action of mercuric acetate. This effect is independent of the excess of iodine chloride and in consequence the modified reagent not only reduces the time required for complete addition, but also reduces, almost completely, the necessity for excess of the reagent. Satisfactory results were obtained with non-conjugated oils and fats having iodine numbers as high as 200.<sup>80</sup>

### Soaps

It has been apparent for some time that the alkalinity of a dilute aqueous soap solution is determined more by the nature of the fatty acids, by concentration and by temperature effects, than by the presence of the small amounts of free alkali usually present in commercial soaps. The  $p_H$  values of dilute solutions of the sodium and potassium soaps of lauric, myristic, palmitic, and stearic acids have been measured at 25° and 50° C. For 0.1-N solutions at 25° these ranged from 9.7 for sodium laurate to 11.45 for potassium palmitate, the potassium soaps being in general hydrolysed more than the sodium soaps. Calculation of the fatty acid concentration in these hydrolysed solutions indicated that the amount was always less than that of the saturated solutions of the acids, and it would appear therefore that free fatty acid can never separate from pure soap solutions.<sup>81</sup> When fatty acid was added to solutions of sodium

oleate and of potassium laurate, even to the extent of 100–150% molecular excess, the solutions were always alkaline.<sup>82</sup> The solubilities of sodium and potassium soaps in 0.004-N KOH have been also measured, the use of this slightly alkaline medium enabling the measurements to be made without the uncertainty caused by the hydrolysis of the soaps and the consequent turbidity of the solutions. The only soaps moderately soluble at room temperatures were potassium laurate, myristate and oleate, sodium oleate and the potassium soaps of coconut oil fatty acids: the other soaps required relatively high temperatures for solution and in this respect there was a marked difference in behaviour between sodium and potassium soaps. The potassium soaps became freely soluble at a fairly definite temperature whereas the sodium soaps, after an initial state of low solubility, became gradually more soluble over a range of temperature. The very low solubility at room temperature of a soap such as sodium stearate is not generally appreciated.<sup>83</sup>

The composition of aluminium soaps has been the subject of two communications, one of which maintains that neither the tri- nor the di-stearate exists. Although most products originally approximate in composition to the di-stearate, it was stated that the stearic acid content is reduced to that of the mono-soap by extraction with solvents such as ethyl alcohol, acetone or ethylmethylketone.<sup>84</sup> On the other hand, it has also been reported that extraction with acetone removes free or loosely bound fatty acid until a product is obtained having the theoretical composition of an aluminium di-soap. The preparation by this method of several di-soaps was described and the melting points of the dilaurate and distearate were recorded.<sup>85</sup> Such extractions must be made in the complete absence of water, otherwise hydrolysis leads to loss of stearic acid, a precaution which was apparently recognised in both these investigations.

The solubility of the heavy metal soaps in mixtures of chloroform and propylene glycol (the so-called co-solvency) has been determined, and of the soaps examined, magnesium soaps were the most soluble, being in fact more soluble than the sodium soaps. In the homologous series of acids, the laurates were the most soluble and the stearates were the least.<sup>86</sup>

A patent has been granted for the preparation of aluminium soaps in which the precipitation takes place from aqueous solution at a controlled  $p_H$  in the presence of a hydrophilic colloid such as glue. It is claimed that a stearate containing about 5% of aluminium can be obtained in this way.<sup>87</sup>

The drying of soap in the form of thin sheets by dielectric heating has been patented: the conveyor constitutes one of the electrodes.<sup>88</sup>

## Detergency

It has been pointed out that for a given detergent, a large number of quantitative determinations such as equivalent conductivity, high frequency conductivity, interfacial and surface tension, osmotic pressure and detergency all show a marked inflexion in the curves obtained when they are plotted against concentration, the inflexions all occurring within

a narrow concentration range. It is clear that some significant change in the nature of the solutions has taken place and large-scale colloid formation has been suggested as the cause. It has been shown that the longer the chain length of the detergent molecule, the lower is this critical concentration. The solubility of soaps is roughly constant up to the temperature at which they begin to dissolve much more readily, and these roughly constant solubilities are, in general, coincident with the critical washing concentrations. When soaps dissolve freely at high temperatures, they are considered to go into colloidal solution, without any substantial increase in the concentration of the long chain ions. It has been postulated therefore that detergent power reaches its maximum at the concentration when colloid formation begins or when further additions of detergent do not dissolve. In neither case is there any further increase in the concentration of the long chain ions in solution and only when maximum detergency has been reached in this way is solubilisation by the colloidal micelle considered to occur.<sup>89</sup> On the other hand, much interesting work has been published on the use of sodium carboxymethyl cellulose products (such as Tylose H.B.R.) as additives or "extenders" to detergent solutions. Considerable economy is effected in the amount of detergent required and it is considered that the function of these "extenders" is to impart colloidal properties to the solutions, thereby increasing their suspending power. Improved soil removal and whiteness of cotton fabrics have been shown to result from the use of relatively small (about 0.5%) concentrations of sodium carboxymethyl cellulose in conjunction with anionic or non-ionic detergents, as well as with soaps. The effect has been obtained in both hard and soft water and also in an artificial sea-water. Suitable mixtures of anionic detergents with alkaline salts and sodium carboxymethyl cellulose have been proved to have detergent powers superior to those of high quality soap.<sup>90</sup> The detergent properties of these cellulose derivatives have been demonstrated in large scale laundry tests on cotton and linen goods.<sup>91,92</sup> In this connection a patented detergent for use in hard water is of interest. The hardness is utilised to produce a water-insoluble, colloiddally dispersed phosphate, the dispersion adsorbing the soil and keeping it in suspension. Sodium tetraphosphates and hexametaphosphates are cited as examples, but the amount added must be less than is required to form the soluble complexes.<sup>93</sup>

The use of non-ionic detergents in the scouring of wool has been described. These detergents cannot hydrolyse in solution like soap and their maximum detergency is obtained in neutral solution, the detergent power being increased by the presence of small amounts of neutral salt, such as sodium chloride. In the scouring of wool and woollen goods, the use of sodium carbonate or soda ash can therefore be limited to the single function of neutralising and removing fatty acids, and its adverse effect on the wool can be correspondingly limited by using a non-ionic detergent in all but the first stage of wool scouring. The second "bowl" therefore contains only non-ionic detergent and 0.5% of common salt. In the scouring of woollen goods oiled only with mineral oil, the use of soda ash is not necessary and excellent results have been obtained with solutions of non-ionic detergent containing a little salt. Freedom from dyeing

troubles caused either by grease or alkali is an important advantage resulting from the application of these processes.<sup>94</sup>

In an investigation into the action of diphasic metal cleaners containing triethanolamine soap in a mixture of mineral spirits and water, it was proved by measurements of the interfacial contact angles that metal was wetted preferentially by the spirits and glass preferentially by the water. This was caused by an excess of oleic acid in the solvent phase and of triethanolamine in the aqueous phase, and the theory was advanced that such a di-phase cleaner will preferentially wet the mineral "soils" with water and leave an adsorbed layer of solvent on the clean metal surface. Lowering of interfacial tension between water and oil does not however necessarily increase the tendency of the aqueous phase to displace oil from a soiled surface. Experiments with steel rings showed that an oil-based soil was effectively removed by agitation with distilled water under standardised conditions whereas a soap solution was effective only when sufficient alkali was present to suppress the hydrolysis of the soap. The increased adhesion of the soil observed with neutral soap solution was caused by fatty acid which had entered the oily layer from the hydrolysed soap. A limited number of tests with synthetic detergents suggested that alkyl-aryl sulphonates exerted a similar but smaller influence, but that sulphated fatty alcohols, cationic detergents, and non-ionic detergents had no effect.<sup>95</sup>

*Analysis of soaps and detergents.*—The colorimetric methods of determination which depend on the complexes formed by anionic detergents with methylene blue and by cationic detergents with bromthymol blue have been known for several years. The solubility in chloroform of either of these complexes has now been used to furnish a partition end-point in the titration of anion-active with cation-active solutions, and the new methods would appear to have considerable importance. The titration is made in the presence of chloroform with a cation-active solution such as M/1000 cetyl pyridinium bromide, the mixture being shaken after each addition. When methylene blue is used as the indicator, the blue complex with the anionic agent is extracted into the solvent layer and, as the titration progresses, the methylene blue is displaced from the complex by the active cation. At the end-point the blue colour is just discharged from the chloroform layer into the aqueous phase. When bromthymol blue is used, the blue complex is not formed until the cation-active agent is present in slight excess at the end of the titration and the first indication of a blue colour in the chloroform layer is taken as the end-point.

The titration is approximately stoichiometric when bromthymol blue is used as the indicator, whereas with methylene blue, an excess of the cationic-active agent is required to produce the end-point. The question is largely one of theoretical interest however, since one anionic detergent can be standardised indirectly against another through the agency of the cation-active solution. Results obtained in this way with purified anionic compounds were virtually stoichiometric whichever indicator was used in the titrations.<sup>96</sup>

Using methylene blue as the indicator, it has been suggested that the end of the titration should be taken as the point at which the two layers

are the same colour when viewed by reflected light. The titration is stated to be stoichiometric when it is carried out in this way and accordingly the molarity of the anionic solution is established when the cetyl pyridinium bromide solution (or other cationic solution) is of known normality. Satisfactory results were only obtained when the chain length of the anionic compound was 8 or more carbon atoms; the position of the polar group did not appear to affect the applicability of the method. Very good end-points were said to be obtained in the titration of water-insoluble sulphonates of high molecular weight.<sup>97</sup>

Methods continue to be published for the determination of detergent power, most of them differing from each other only in practical details, but mention should be made of a suggested method for measuring the efficiency of detergents for dish washing. The detergent power of the solutions was measured by their ability to clean glass wicking that had been soiled in an appropriate manner. Soil "pick-up" was also investigated and the method would seem to have definite advantages over the more usual detergent tests on glass slides.<sup>98</sup>

A method for the titrimetric determination of heavy metal soaps has been described, which is similar to a method previously proposed for the determination of the soaps of the alkali metals. The soaps are dissolved in a mixture of propylene glycol and chloroform, and the titration is made with perchloric acid using thymol blue as the indicator.<sup>99</sup>

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# GLASS

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ALTHOUGH no outstanding developments have occurred during the year, 1948 has been a year of steady progress in the glass industry. The work reviewed in this report has been carried out mainly in Britain, France, and America, and international co-operation on problems relating to glass was stimulated by a meeting of the International Commission on Glass, the first meeting for many years. The meeting was the occasion for a symposium on the "Nature and Constitution of Glass," but publication of the papers presented was too late for inclusion in this review.

## The constitution of vitreous systems

As in previous years, a considerable amount of work on the constitution of glasses has been published, some papers being of a general nature and others being concerned with particular aspects of the structural theory. General accounts of the structural theory and of the laws governing glass formation have been given by A. Winter-Klein<sup>1</sup> and K. H. Sun.<sup>2</sup>

J. E. Stanworth<sup>3</sup> has examined the Zachariasen random network theory in relation to recent experimental data on glass formation, consideration being given to those oxides which are regarded as glass formers on the network theory. It is concluded that the criteria for glass formation in oxide glasses put forward by Zachariasen still provide an excellent guide. Under certain conditions the  $\text{Al}^{3+}$  ion can be an effective glass former, but experiments show that calcium aluminate glasses can be formed only in very small, quickly cooled samples. In considering the behaviour of other cations, Stanworth discusses the behaviour of lead which may be introduced in large quantities into glass-forming oxides. In such glasses, the silicon tetrahedra are probably linked by lead atoms. In special cases, ions with outer shells of  $(18 + 2)$  electrons such as  $\text{Pb}^{2+}$ ,  $\text{Tl}^{+}$ , and  $\text{Bi}^{3+}$  are capable of acting as network formers and ions with shells of 18 electrons are capable of forming substantially covalent bonds with neighbouring oxygen atoms.

The stability of glasses containing high proportions of lead has also been considered by K. Fajans and N. J. Kreidl,<sup>4</sup> who suggest that the simple theory of network former and network modifier is inadequate for such glasses because the  $\text{Pb}^{2+}$  ion does not fit the usual concept of a glass former. From a study of the influence of cations of noble gas character on the optical refraction of silicate glasses, it is concluded that all such cations affect the refractive power, the electron cloud of the oxygen ion being distorted in the cationic field. The polarising action of such strong fields as those of  $\text{B}^{3+}$  and  $\text{Si}^{4+}$  accounts for the stability of many glasses and is favourable for glass formation. The Lorentz-Lorenz molar refraction formula may be used to determine the refraction of  $\text{O}^{2-}$  and the values thus derived can be considered as a measure of the tightness

of the electronic shells. The effects on the apparent molar refraction of the oxygen ion have been calculated for many cations and on this basis it is possible to differentiate between network formers and network modifiers. While the lead ion  $\text{Pb}^{2+}$  is not of noble gas character, it is itself easily polarisable and it is the deformation of this cation on the anionic field which probably accounts for the stability of lead silicate glasses. In tetragonal  $\text{PbO}$ , four of the eight oxygen ions surrounding the  $\text{Pb}^{2+}$  ion are closer than the other four and this asymmetry is connected with the high polarisability of  $\text{Pb}^{2+}$ . If it be assumed that the same lack of symmetry is also present in lead silicate glasses, then it is possible to understand the glass-forming ability of the lead ion.

A. Dietzel and H. A. Sheybany<sup>5</sup> have investigated the physical and chemical properties of simple alkali-silicate glasses in order to obtain further information concerning the filling of the structural holes in the silica network. It is found for example that chemical solubility increases slowly up to a certain critical alkali content which is dependent on the particular alkali and it is considered that the critical alkali content corresponds to a structure in which every alkali ion ceases to be enclosed by  $\text{SiO}_4$  groups. A study of the thermal expansion curves shows that the structure is least affected by temperature in the case of the ion with the strongest field. Above the transformation point, the expansion curves show a definite change at a critical alkali content and above these critical values, the expansion coefficients are substantially constant. At this stage, it is considered that the  $\text{SiO}_4$  groups become separated and that a further increase in alkali content has no appreciable effect.

H. A. Sheybany<sup>6</sup> has extended the investigation to a study of more complex glasses which were obtained by gradual replacement on a molecular basis of the single alkali component of each of the binary glasses by one of the other alkalis. The experimental results show that the density is not a linear function of the composition which may be explained either by a change in the polarisation following the interaction of the electric fields of the alkali ions or by the purely mechanical effect of the packing of the alkali ions of different size. The variation of chemical solubility with alkali content was found to depart from the linear relationship in a similar manner and is considered to be a natural consequence of the packing effect of the ions. On the other hand, the coefficient of expansion bore a linear relationship to composition, but since the expansion is a consequence of the thermal oscillation of the ions, the presence of structural cavities and the packing of ions in the cavities does not affect the phenomenon.

In a further investigation, Sheybany<sup>7</sup> has built up a series of molecular models in which the various ions were represented by steel balls of different sizes. While the experimental results for density obtained on the models represent the behaviour of binary glasses, agreement is not good for the ternary glasses. The effects observed are attributed to a modification of the polarisation of the alkali ions in the mixed glasses.

It is recognised that any structural theory must explain adequately the viscosity-temperature behaviour of glasses and it has long been suggested that the change of viscosity with temperature could be attributed to a change in the state of aggregation of molecular groupings.

J. E. Stanworth<sup>8</sup> has considered the viscosity-temperature relationships for glass on the basis of the theories of Frenkel and of Eyring and deduces expressions for the energy of activation which indicate that changing entropy and changing activation energy are responsible for the viscosity changes. Quantitative estimates based on the theory suggest that large molecular aggregates do not exist and the moving particles do not appear to be much larger than single molecular size.

K. H. Sun<sup>9</sup> has discussed the acidity and basicity of glasses, pointing out that according to the Lewis theory, neutralisation in an acid-base reaction is due to the formation of a covalent bond between acid and base while in glass formation, it is the formation of a covalent bond between the oxygen from the base and the more strongly positive atoms. The weaker the bonding between an element M and oxygen O, the stronger will the oxide act as a base and from a knowledge of the various M-O bond strengths it is possible to set up an acidity-basicity scale. Thermal data involved in the formation of glasses provide experimental values which automatically take account of the uncertain geometric factors and the charge distributions required for the evaluation of ionic potentials. From the dissociation of MO in glass and the oxygen co-ordination of M, Sun evaluates the bond strengths which are found to agree well with the behaviour of various components in glasses.

While the generally accepted structural theory denies the presence of crystal groupings in glasses, some work recently reported by G. S. Bachman<sup>10</sup> suggests that a stage intermediate between the crystalline and the truly vitreous states can exist. By means of infra-red transmission spectra, Bachman examined the structures of powdered silicate glasses prepared by melting crystals such as albite and anorthoclase both of which have substantially the same formula  $\text{NaAlSi}_3\text{O}_8$ , microcline and orthoclase which have the formula  $\text{KAlSi}_3\text{O}_8$ . If composition alone determines the structure of the glasses produced by melting these crystals, the structure of albite glass should be independent of temperature apart from slight differences which might arise from differential volatilisation of the components. Identical infra-red transmission curves would also be expected for microcline and orthoclase glasses. On the other hand, if the structures of the glasses bear any relationship to the crystals from which they are melted, differences between glasses of the same composition would be expected. The experiments which Bachman has reported suggest that the glasses melted at  $1400^\circ\text{C}$ . had infra-red spectra which bore some resemblance to those of the parent crystals but the glasses were more nearly alike than the original crystals. When melted at  $1500^\circ\text{C}$ ., the glasses were more nearly alike than the glasses melted at  $1400^\circ\text{C}$ . This work may be regarded as of an exploratory nature and it is evident that further investigations should be undertaken as they have an important bearing on the general structural theory.

Glass technologists working in the field of glass compositions can often obtain valuable guidance from the phase diagrams which are to be found throughout the literature. F. P. Hall and H. Insley<sup>11</sup> have performed a valuable service in collecting together the published data on phase diagrams of systems containing one to five component oxides and systems containing non-metal oxides, halides, or water. Most of the

diagrams contained in the collection are now regarded as classical and the collection will form a convenient one for reference. The authors include a general discussion on phase diagrams and their interpretation and they outline the methods for determining high temperature heterogeneous equilibria.

According to A. Q. Tool,<sup>12</sup> the unusual density changes which occur when silica-rich borosilicate glasses are subjected to heat-treatment may be explained on the supposition that the glass is made up of two components, a phase consisting mainly of silica and a phase consisting of a borosilicate glass containing a moderate amount of silica. The silica phase forms a rigid network throughout the body of the glass at temperatures sufficiently high to maintain the other component in the liquid state. The borosilicate phase forms a rigid network at a lower temperature and on account of its higher expansion coefficient will compress the high silica component. The changes in density accompanying various heat-treatments can be adequately explained on this hypothesis.

Tool and Saunders<sup>13</sup> have reached similar conclusions from a study of the thermal expansion effects shown by some Pyrex glasses.

The structures of opal glasses are of particular interest to the glass technologist since they frequently consist of some form of crystalline phase or phases within a vitreous matrix. T. F. Bates and M. V. Black<sup>14</sup> have reported some interesting results obtained by an examination of freshly fractured surfaces of opal glasses by the electron microscope using the replica technique. Calcium and sodium fluoride glasses showed well defined crystalline forms and the numbers of crystals per sq. cm. of surface were of the order of  $10^7$ – $10^8$ . Another interesting feature of such glasses was the number of gas bubbles present. These varied in number from  $10^8$ – $10^9$  per sq. cm. of surface. The steps in the preparation of the negative replica are shown and an excellent series of photographs of various surfaces is included. The work indicates that the electron microscope can be a valuable tool in the elucidation of glass structure.

### Glass-making materials and glass compositions

From time to time, W. A. Weyl<sup>15</sup> has published collected data on the important constituents of glasses and during the past year has been responsible for a series of papers on the chemistry of boric oxide and its rôle in glass technology. Detailed information is given on the structural aspects of boric oxide glasses, the effect of boric oxide on physical and chemical properties, and the part it plays in glass melting. An extensive bibliography is included in the paper.

Weyl<sup>16</sup> has also reviewed the present knowledge of phosphate glasses. After an historical summary and a comparison of the structures of  $P_2O_5$  and  $SiO_2$ , Weyl examines the range of compositions and discusses the use of phosphate glasses for special purposes, optical properties, high ultra-violet transmission, heat-absorbing glasses, fluorescent glasses and glasses resistant to hydrofluoric acid.

Over the past few years, the General Research Laboratories of the Owens Illinois Glass Co. have published several papers on the physical and chemical properties of various series of glasses. During the year, a paper on a series of glasses in the system  $Na_2O$ – $SrO$ – $Al_2O_3$ – $SiO_2$  in

which strontium oxide was substituted in turn for each of the other constituents has appeared.<sup>17</sup> Altogether, 27 glasses were examined and comparison made with a similar series of glasses in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . The same laboratory was responsible also for a paper on the effect of boric oxide on the properties of soda-dolomitic lime-silica glass, a systematic substitution of  $\text{B}_2\text{O}_3$  for  $\text{CaO.MgO}-\text{Na}_2\text{O}$  and  $\text{SiO}_2$  being made in two base glasses.<sup>18</sup> The amount of experimental data given in these two papers is too extensive to be summarised in this report.

The rare earths are widely used in special types of modern glasses and their applications and the properties of the glasses containing such materials have been summarised by M. Foëx.<sup>19</sup> Such summaries are very valuable as the information is often widely scattered in the literature.

The choice of a glass composition for any particular purpose is determined by many factors which depend on economics, the availability of raw materials and the results of research into the many aspects of the glass melting process. It is not surprising therefore that over a period of years, many changes can occur in mixtures for container glass and the review by H. Moore and A. K. Lyle<sup>20</sup> of glass compositions in the American glass container industry for the years 1932-46 provides an interesting study. As might be expected there is a continuous trend to more complex glasses. A. G. Allen and A. K. Lyle<sup>21</sup> have brought the review up to date by providing data for the year 1947.

### Glass melting

In the practice of glass making, a knowledge of the fundamental physical and chemical processes of glass melting is of great importance but compared with other branches of glass technology the subject receives little attention. It is gratifying to record therefore that a greater number of papers dealing with this subject have been published during the course of the year than for many years past. Much of our present knowledge is due to the studies of H. Jebsen-Marwedel, whose work has been denied to English readers for some years and his recent papers are therefore to be welcomed. Jebsen-Marwedel has always emphasised the importance of surface tension in the process of glass melting and in a recent paper<sup>22</sup> has discussed the part it plays, together with adhesion and osmosis in the homogenising of glass. In a second paper, Jebsen-Marwedel<sup>23</sup> discusses the chemical reactions, the processes of solution and the formation of bubbles in glass melting, processes which occur at the interfacial boundaries in a heterogeneous mixture. Again, the importance of surface tension is discussed and the behaviour at the interfaces of soluble and insoluble liquids in contact with one another is illustrated by a series of photographs. Jebsen-Marwedel suggests that the origin of defects in the finished product can often be traced by a microscopic examination of the interfaces. Jebsen-Marwedel and K. Dinger<sup>24</sup> have described a novel method for determining the degree to which a glass has been freed from gases in the melting process. The glass is heated in a gradient furnace under a reduced pressure and the temperature at the boundary at which bubbles are evolved is regarded as the criterion of the degree of refining. It is concluded that glasses which show only slight variations in the

equilibrium temperature for variations in pressure can be regarded as the best glasses from the point of view of refining.

The heat of formation of glasses is another subject which has received little attention from chemists and the work of L. Shartsis and E. S. Newman<sup>25</sup> suggests a method for investigating the problem. These workers have studied the heats of solution in various acids of a series of glasses and of their component oxides in the systems  $\text{PbO-B}_2\text{O}_3$  and  $\text{PbO-SiO}_2$ . From the data thus obtained and from the heats of fusion, the heats of reaction in glass formation of the component oxides in both the amorphous and crystalline states were calculated.

The question of the effect of sand grain size in glass melting is one which has to be examined by the glassmaker and much of the data published on the subject is contradictory. F. Gjesmoe<sup>26</sup> has described his experience using finely crushed quartz as compared with Belgian sand in melting a soda-lime-silica glass in a tank furnace and shows that the quartz mixture melted and refined more quickly. The carry-over of dust into the regenerator chambers was remarkably low.

In recent years, the possibility of melting glass on a commercial scale by electrical conduction through the glass has engaged the attention of glass technologists and, in some countries, electrical melting is being practised on a large scale. The technical and economic aspects of electric melting have been discussed by Y. R. Cornelius,<sup>27</sup> who has had considerable practical experience of the problems involved. A general review of methods of melting glass electrically and of some of the associated problems has been given by L. Dubrul.<sup>28</sup> An account of the experiments on glass melting in electric furnaces which have been carried out in Spain has been given by J. Finger.<sup>29</sup> The construction and dimensions of the furnaces, the electrical arrangements and the types of glass melted are described.

### Furnaces and refractories

The papers published by I. Psychès on the convection currents in glass tanks which were reviewed in the 1947 report have now appeared in English translation by S. R. Scholes and L. Sutton.<sup>30</sup>

Some years ago the Furnace Committee of the Society of Glass Technology put forward a formula for assessing the thermal performance of glass tank furnaces. Although not regarded as final, the formula provided a basis of comparison for furnaces of widely differing kinds and from time to time the results of applying the formula to specific furnaces have been published. H. Brøndum-Nielsen<sup>31</sup> has now put forward proposals for an extended form of the formula based on the statistical examination of the results obtained by Moxon, Winks, and Dudding on a furnace fired by coke-oven gas.

In previous reports, the papers published by R. Halle and W. E. S. Turner on the temperature gradients in glass-melting furnaces have been reviewed. In one of the papers, Halle and Turner described their measurements on the vertical temperature gradients in an experimental tank. C. E. Gould<sup>32</sup> has now correlated these measurements with measurements obtained in a full-scale tank and has found that the same exponential relationship between temperature and depth covers both sets of

measurements. Gould uses his formula to calculate the mean temperature and the bottom temperature of tanks of 30 in. depth containing glass with various amounts of iron oxide and deduces the effects of iron oxide content on the life of the bottom of the tank.

The problem of the attack of refractory materials by molten glass in tanks is one of great complexity. Above the glass level, the refractories are attacked by vapour and by erosion by particles borne by the flame. Below the glass there is corrosion and erosion. In a paper dealing with a study of refractory attack, K. E. Seal<sup>33</sup> has attempted to develop a hypothesis of the mechanism of corrosion from a petrographic examination of the refractories after service. Representative samples were taken from various parts of the tank structure so as to include all the different kinds of attack produced by the melting batch, by the glass, and by the vapour. The results of the examination of the samples are reported and many photographs of the effects of corrosion are given.

A novel method of testing the corrosion and fluxing of refractory glass mixtures based on the assumption that a refractory brick which gives a brick-slag mixture having a high range of viscosity will be less readily attacked by the slag than one giving a low viscosity range, has been put forward by J. F. Hyslop, J. Stewart, and N. Burns.<sup>34</sup> A rapid test of the slag resistance of a brick consists in heating on the surface of the brick a small cube composed of 80% brick, 20% slag, on top of which is another cube composed of 20% brick and 80% slag. The viscosity of the melted cubes and the degree of attack are observed qualitatively. The method was to study the attack of a standard soda-lime glass, a commercial borosilicate glass and an alkali lead silicate glass with a wide range of refractories at a temperature of 1450° C. Photographs of the test-pieces are given in the paper.

An electrically-heated tank-furnace for testing the resistance of refractories to the action of molten glass has been described by J. C. McMullen.<sup>35</sup> R. Tatincloux<sup>36</sup> has reviewed the various types of glass tank refractory which have come into use over the past 30 years. The review deals in particular with electrocast refractories such as Monofrax, Corhart, and refractories containing zirconia.

## Annealing

The classical work of Adams and Williamson has long been used in the glass industry as the basis for annealing rates for glassware; it was shown by them that the basic assumption made by F. Twyman, that the rate at which strain disappears at constant temperature obeys Maxwell's exponential law is only an approximation to the truth. In practice, the rate of strain disappearance is more rapid in the initial stages than given by the exponential law and several attempts have been made in the past to explain the reasons for the departure from the law. For example, J. T. Littleton and H. R. Lillie have suggested that the viscosity of the glass itself is changing during the annealing process and approaches asymptotically a value characteristic of the temperature and of the glass itself. G. O. Jones<sup>37</sup> has now suggested that during the annealing process, delayed elastic strains are in process of development at the same time as stress is being released by viscous flow. The stresses which give rise

to the delayed elastic strains are the ordinary unrelieved stresses remaining in the glass at any stage of the annealing process. They develop during annealing because the process involves a rise in temperature which in turn leads to an increase in the magnitude of the delayed elastic strain corresponding to a given applied stress. The strain-time relationship for a piece of glass under an applied external stress can be divided into three parts (a) an instantaneous elastic strain, (b) a Newtonian viscous flow, and (c) a delayed elastic strain governed by a decay function of time, of limiting value unity. Jones considers the stresses in a strained piece of glass rapidly heated from room temperature to such a temperature that the ratio of the delayed elastic strain to the instantaneous elastic strain is finite, and shows that the compressive and tensile stresses are reduced on account of the delayed elastic strain alone. At temperatures approaching the annealing temperature the effect due to the delayed elastic strain is shown to be comparable with that due to viscous flow alone. The process of annealing seems to be so complex that with the available data on the phenomenon of delayed elasticity, it is impossible to forecast the true laws of annealing. It seems evident, however, that the delayed elastic effect will have a considerable influence on the annealing rate.

G. D. Redston and J. E. Stanworth<sup>38</sup> have developed simplified annealing schedules based on the Maxwellian equation for rate of stress release. As stated above, this equation is only an approximation to the truth so far as glass is concerned but for most practical cases, an assumption of the simple law leads to adequate annealing schedules. The schedules given by Redston and Stanworth should be valuable to those workers not familiar with the problem of annealing.

The validity of the empirical law for rate of stress release has also been examined by S. M. Cox,<sup>39</sup> who shows that while the law is applicable only over a limited time range, it is adequate in practice since it holds over just that time range applying in industry.

Many modifications of the exponential equations for the rate of change of physical properties towards their equilibrium values have been proposed from time to time. P. W. Collyer<sup>40</sup> has applied several of these equations to his experimental results for the rate of approach of the refractive index of borosilicate glass to equilibrium and finds that an equation of the form  $\frac{dn}{dt} = Q(n_e - n)e^{n/p}$  best fits the results. ( $Q = MKe^{T/g}$ ,  $t$  = time,  $T$  = temperature,  $n$  = refractive index at time  $t$  and  $n_e$  = equilibrium index, and  $M$ ,  $K$ ,  $p$ , and  $g$  are constants.) The equation is similar to that proposed by A. Q. Tool.

The annealing of optical glasses is a twofold problem of reducing mechanical stresses to a minimum and developing a refractive index to a constant value both throughout a given sample of glass and from one sample to another. The absolute value of the refractive index is dependent on the annealing temperature employed and for every annealing temperature there is an equilibrium value for index. A. Q. Tool, L. W. Tilton, and J. B. Saunders<sup>41</sup> have published values for refractive index, dispersion and density for several optical glasses which were allowed to reach equilibrium at various temperatures and then cooled to room

temperature. The density and refractive index were found to increase linearly with falling equilibrium temperature. Data on the temperature coefficients of dispersion are also given.

### Analysis and testing of glass

As in previous years, many analytical procedures have been published which are adaptable to glass analysis but for the purposes of this review only a few have been selected as being of special interest.

J. T. Jones<sup>42</sup> has investigated the use of zinc uranyl acetate for the determination of sodium oxide in glasses and has evolved a rapid and precise method for routine analysis. The method can be used in the presence of almost every other constituent likely to occur in glasses and the risk of loss of sodium in removing other constituents is eliminated. The *o*-phenanthroline method for the estimation of iron has been adapted by J. J. Diamond<sup>43</sup> to the determination of iron in glass sands. The method of Gentry and Sherrington for the estimation of lead as iodate in glass analysis has been examined by P. M. C. Proffitt and R. C. Chirnside,<sup>44</sup> who have found that the method is likely to lead to errors owing to the presence of iron and titanium in the precipitates. It is concluded that the method is applicable only to glasses low in iron.

A comprehensive treatise on the applicability of colorimetric methods for the rapid and complete analysis of silicate materials has been published by R. Hedin.<sup>45</sup> The methods studied refer to the determination of all the main components of silicates, a photo-electric colorimeter being used. Details of preparation of the solutions are given and it is claimed that by using the time-schedule laid down, a total analysis of a silicate can be completed in eight hours.

A novel method of testing the resistance of glasses to hydrofluoric acid has been described by E. Darmois.<sup>46</sup> The method depends upon the fact that a mixture of tartaric acid and antimony fluoride alters in optical activity after contact with the glass surface due to the reaction with the glass of small amounts of  $F^-$  and  $H^+$  resulting from hydrolysis of the antimony fluoride. The change in optical activity was found to be related directly with the weight loss from the glass.

Of the physical testing methods, the rapid non-destructive method for refractive index by immersion in a hollow  $60^\circ$  prism and the use of a divided circle spectrometer may be mentioned.<sup>47</sup> A. A. Padmos and J. de Vries<sup>48</sup> have given an account of the formation of stresses in glass and the methods of measurement. These authors describe a method for testing the suitability of glasses and metals to be fused together in which the samples are fused to a standard glass and the combination observed in polarised light.

### Mechanical properties

Most of the work on mechanical properties published during the course of the year has been concerned with the mechanical strength of glass, and apart from the value of their work in increasing our knowledge of this important subject, many workers have attempted a new approach using the theories of physical chemistry. According to the Griffith theory of brittle rupture, a solid is an elastic continuum containing

microscopic flaws and the failure of the material under a stress less than that corresponding to the theoretical strength is attributed to the enhancement of the stress in the locality of the flaws rather than to any intrinsic weakness in the material itself. S. M. Cox,<sup>49</sup> in discussing the phenomena associated with glass rupture applies the kinetic theory in assuming that the thermal energies of the atoms are distributed according to the Maxwell-Boltzmann law and is led to the conclusion that there is a finite probability that some of the atoms have sufficient energy to cause a local discontinuity and consequently local stress enhancement. Cox suggests that the statistical outcome of the atomic properties of frequency and energy of vibration lead one to expect glass under tensile stress to exhibit the phenomena which are in fact observed. He shows that the theory yields qualitative results which accord with the experimental results obtained by various workers and suggests that it provides a common background upon which the various features of glass rupture can be co-ordinated.

W. A. Weyl<sup>50</sup> has adopted a physico-chemical approach in a discussion of the mechanical properties of glass. He suggests for example that a flowing material can be treated in the same way as a mixture undergoing chemical change and that the equations for absolute reaction rates can be applied to the viscous flow of glasses and to the diffusion of gases through glass. The vitreous state is characterised by a random arrangement of ions, and the properties of glasses are governed by the wide spread in bond strength, intermolecular distances and co-ordination numbers. The viscous properties and the tensile strength phenomena are the result of the variations in bond strength. Many of the phenomena characteristic of rigid glass can be attributed to the severing of the weaker bonds by mechanical or electrical forces leading to a redistribution of the force over the remaining bonds. Elastic after-effect problems are associated with the time-delays necessary for such redistribution of the forces. Weyl discusses many other physical properties of glass and although the paper is of a general nature it suggests another method of approach to some of the problems associated with the physical properties of glasses.

The mechanism of fracture of glass and similar brittle solids has been examined by N. W. Taylor,<sup>51</sup> who has treated the problem as a chemical reaction rate. It is probable that most materials are brittle at the time of actual rupture because the atomic and molecular mechanisms which normally adjust themselves to the applied stress are exhausted just prior to the instant of fracture. A model is used to deal quantitatively with the slow process preceding fracture and an equation for time of fracture is deduced which has the same form as the empirical equation proposed by Glathart and Preston.

The theory of rates of chemical reaction has also been used by E. Saibel<sup>52</sup> in a study of the time effect on the fracture of glass. The rate at which external loads are applied and the effect of the breaking of the structural bonds on the unbroken bonds is considered. Saibel derives a relationship between the time to fracture and the rate of loading which involves only two constants which are dependent on temperature.

Experiments on the fracture of soda glass rods under four point bending

have been reported by C. Gurney and S. Pearson.<sup>53</sup> In one series of experiments, the load was increased at a constant rate until fracture occurred and in another series, the times of fracture under a range of constant loads were determined. Each series of tests was made under three sets of conditions, one with static specimens and the other two with specimens rotating at 14 and 10,000 r.p.m. It was found that under cyclic loading, the glass did not fracture appreciably faster than it did under static loading and this is considered to be in accord with expectation if the fatigue is due to crack spreading rather than to deterioration of inherent strength.

The delayed fracture of various materials (including glass) in contact with different media under tension, torsion, and compression has been investigated by C. Gurney and Z. Borysowski.<sup>54</sup> They consider that the gradual spreading of cracks is caused by the preferential attack by the surrounding media of the highly stressed material at the ends of the cracks. For brass and glass under tension or torsion, fracture occurred in not greatly differing times when the materials were subjected to the same maximum principal stress. The results obtained with glass were in agreement with the theoretical work of Preston and Glathart.

The modification of the strength of glass by wetting with various agents has also been studied by F. Canac and J. H. de Chanville,<sup>55</sup> who show that contact with water reduces the bending strength while paraffin and ethyl alcohol increase it. These authors discuss also the various types of fracture and of deformation.

The relationship between Young's modulus and the structure of glass has been discussed by J. Gillod.<sup>56</sup> E. H. Poncelet<sup>57</sup> has also discussed the relationship between glass fracture and structure in a paper which surveys in detail the fundamental ideas of fracture in solids.

A. J. Holland<sup>58</sup> has reported the results of an investigation into the effect of low temperatures on the strength of glass. He found that when the temperature is lowered from 17.5° to - 40° c., the modulus of rupture by loading is increased by 20-25% and the modulus of rupture by impact is increased by 17%.

In their latest contribution to the subject of mechanical strength J. L. Glathart and F. W. Preston<sup>59</sup> have used an analytical treatment to deduce expressions which cover the breakage of glassware under service conditions. The breakage of a piece of glassware is not due to impact *per se* since the article will survive many impacts and finally succumb to a minor one. While in use, ware is subjected to scratching and abrading which prepares the glass for breakage. Glathart and Preston suggest therefore that, in general, breakage involves two independent processes, the "vulnerating" process and the final impact. On this assumption a mathematical treatment is developed which yields a mortality curve showing the relationship between rate of breakage and the age of the article in service. This curve is shown to represent accurately, the results of a service test on glass tumblers. It is also shown that impact strength as determined by laboratory tests declines with service age in a manner consistent with the assumptions made. Many other important conclusions are reached in this paper. The experiments show, for example, that impact as such does not affect the glassware so far as its behaviour to

successive impacts is concerned and also that time and weathering alone do not affect strength. The ultimate criterion is the amount of abrasion which the ware receives in service. This paper is an excellent example of operational research and the mathematical treatment alone should be of interest to the research worker.

The increased strength of glass fibres as compared with massive glass is a well known phenomenon and forms the subject of investigation from time to time. J. J. Bikerman and G. H. Passmore<sup>60</sup> have made a statistical analysis of the ultimate tensile strength, the total elongation and modulus of elasticity of fibreglass. It is concluded that while Young's modulus is almost independent of length, the ultimate tensile strength increases with decreasing fibre length. This is probably due to the lower probability of a point of weakness in the shorter fibre. The high strength of fibres as compared with massive glass is attributed to the favourable orientation of flaws in the drawn glass and not to a different molecular arrangement.

The effect of shape on the stress systems set up by thermal gradients has been the subject of theoretical investigation by J. B. Murgatroyd,<sup>61</sup> and his results are applied to the problem of the thermal endurance of cylindrical glass containers. The stress systems at the mouth and at the junction of the cylindrical wall and base are considered, but in the present state of theoretical knowledge and experimental data, only a qualitative assessment is possible. In the second part of the paper, the results of the theory are compared with the experimental results obtained on containers.

Turning now to the work on other mechanical properties, a description has been given of the method of measuring specific gravities to an accuracy of 0.0001 using only a fragment of material.<sup>62</sup> Such methods are of particular interest to the glass technologist as the routine measurement of specific gravity is being used to an increasing extent for quality control during manufacture. A knowledge of the viscosity of glass at high temperatures and particularly the effect of small changes in glass composition is frequently required by the glass technologist. The measurement of this property is difficult and cannot be rapidly accomplished and such data as those published from time to time by M. V. Okhotin are therefore valuable. Okhotin<sup>63</sup> has recently published data for the approximate calculation of the viscosity of glasses in the system  $\text{SiO}_2\text{--CaO--Na}_2\text{O--MgO--Al}_2\text{O}_3$ . The measurement of viscosity in the annealing range is also important and methods of measurement by fibre elongation, by torsional bending of a cylindrical rod and simple bending under load have been discussed.<sup>64</sup>

J. P. Poole<sup>65</sup> has reported the results of an experimental investigation of the viscosity of glasses in the systems  $\text{K}_2\text{O--SiO}_2$ ,  $\text{Na}_2\text{O--SiO}_2$ , and  $\text{K}_2\text{O--Na}_2\text{O--SiO}_2$ , and concludes that viscosity is not an additive function of composition. The results show the practical advantages that may be gained in increasing the working range of a glass when some of the sodium oxide content is replaced by potassium oxide.

The surface tensions of glasses in the systems  $\text{PbO--B}_2\text{O}_3$  and  $\text{PbO--SiO}_2$  have been determined by L. Shartsis, S. Spinner, and A. W. Smock,<sup>66</sup> using the anchor ring method. These workers found that the surface

tensions are related to the changes in composition on heating due to volatility of the components and a correlation was found between the composition-expansibility curve and the curve relating composition with the temperature coefficient of surface tension. H. Jebben-Marwedel and K. Dinger<sup>67</sup> have discussed the effect of furnace atmosphere on surface tension measurements and point out that under reducing conditions the surface tension of glass may be 20% higher than under oxidising or neutral conditions.

A reflectometer for measuring the effects of abrasion and of corrosion by external agents such as water, steam, and various chemicals has been described by F. Canac and R. Montel.<sup>68</sup> A useful review of the work which has been done on the chemical attack on glass by various liquids has been given by F. W. Klaarenbeek.<sup>69</sup>

### Electrical properties

The possibility of producing electrically conducting glasses has been investigated by R. L. Green and K. B. Blodgett,<sup>70</sup> who find that glasses containing lead, bismuth, and antimony become conductors on chemical reduction with hydrogen. The magnitude of the conductivity depends on the nature and on the amount of the reducible oxides, on the temperatures at which reduction is carried out and on the electrical influence of the non-reduced parts of the glass. The conduction occurs in a surface layer about 0.001 in. thick. The presence of alkali ions appears to decrease the conductivity, indicating that the conducting mechanism is dependent on the nature of the glass structure.

The development of soft glass enamels and some of their electrical applications have been described by A. E. Dale and J. E. Stanworth. Such enamels are useful for fusing together glass parts without deformation of the glasses themselves and have many applications in glass apparatus for electrical work.

The magnetic susceptibilities of borax glasses have been investigated by S. K. Majumdar,<sup>72</sup> who concludes that crystallites are present in the glasses.

### Optical properties and coloured glasses

Most of the work in this section published during the year has been concerned with coloured glasses of various kinds. J. M. Stevels<sup>73</sup> has been responsible for a review of knowledge on the relationship between glass structure and colour in which the structural positions of the various colouring ions are discussed.

Experiments which suggest that cobalt can exist in the elemental form as a colloidal suspension in glasses have been described by M. Fanderlik and F. Schill.<sup>74</sup> Cobalt is known in glasses as a network former giving the well known blue colour and as a network modifier giving the red and pink colours of aqueous solutions of cobalt salts. These authors have found that under the strongly reducing conditions obtained by using silicon in the melt, cobalt could be reduced to the elemental form, the particles being detectable by the ultra microscope.

The reduced glass in the quickly cooled state was colourless and a reddish-brown colour could be developed on heat treatment. Spectral-transmission curves are given for several experimental melts containing iron and cobalt separately and in combination, with and without reducing agents.

A comprehensive account of the effect of colouring oxide additions on the spectral transmission of soda-lime-silica glass has been given by G. S. Bachman.<sup>75</sup> Oxides of vanadium, chromium, copper, iron, cobalt, nickel, neodymium, praseodymium, samarium, and uranium were used in three different proportions and their effects on the ultra-violet, visible, and infra-red transmissions were determined. The data were presented in the form of curves relating percentage internal transmission for 2-mm. glass thickness to the wavelength. The absorption bands are classified according to their origin and the absorptive power of the various oxides are compared with one another. The paper contains a useful review of the literature. V. Ctyroky<sup>76</sup> has published the results of a study of soda-lime-silica glasses and soda-potash-lime-silica glasses containing varying amounts of ceria, vanadium oxide, titanium oxide, and chromium oxide, separately and in combination with one another and with cobalt oxide. The purpose of the work was to produce glasses transparent to visible radiation but which absorb strongly in the ultra violet. The transmission curves published in the papers show that excellent results can be achieved.

The colours produced by various concentrations of iron in a soda-lime-silica glass made under varying degrees of oxidation and reduction have been studied by J. W. Forrest, N. J. Kreidl, and T. G. Pett.<sup>77</sup> The methods available for the establishment of accurate standards of spectral and luminous transmittances of various shades of industrial eye protective glasses have been described by R. Stair.<sup>78</sup> Comprehensive data are given for a large number of American eye protective glasses. The uses of the glasses in industry and in the laboratory are discussed. The infra-red absorption of glasses is a matter of some importance and it is well known that the transmission curves for most glasses contain an absorption band at 2.7-3.0  $\mu$ . Many theories have been advanced for the origin of this absorption band, but the recent work of A. J. Harrison<sup>79</sup> suggests that it is due to the OH vibrational absorption. Harrison prepared glasses in such a way that water was removed to varying degrees and it was found that the resulting glasses gave increasingly higher transmission in the infra-red.

H. G. W. Harding<sup>80</sup> has given data for the properties of a blue glass which may be used with tungsten filament lamps for obtaining approximate colour temperatures and intensities of light sources equivalent to higher temperatures than the lamp itself.

Opaque glasses of the diffusing type have many applications, and glasses in this category hold an important place in the glass industry. Because of their importance such glasses have been studied extensively over the last 30 years, and the published results of these studies have now been collected together by C. H. Commons<sup>81</sup> in a review of the past and present practice and the theory of opaque glasses. Opacity in glasses may arise in different ways and Commons describes each of these,

references being made to authoritative literature in each case. A comprehensive table of the batch compositions and a table of the theoretical compositions of the same glasses is given; consideration is given to the theory of the relationship between the refractive indices of the glassy phase and the dispersed phase and the effective size of the dispersed particles are discussed. Methods of improving opacity are outlined in the light of our present knowledge of the subject.

During the past ten years a considerable amount of research has been done on the development of new optical glasses of high refractive index coupled with low dispersion. Such glasses have been made possible commercially on account of the increasing availability of such raw materials as lanthanum and thorium oxides, which are used to replace barium in glasses of the dense barium crown type. A quantitative investigation of the effect on refractive index, dispersion and liquidus temperature of replacement of barium oxide and silica in a three component glass  $\text{SiO}_2$  35.5%,  $\text{B}_2\text{O}_3$  10.7%, and  $\text{BaO}$  53.8% by various oxides, has been made by E. H. Hamilton, O. H. Grauer, Z. Zabawsky, and C. H. Hahner.<sup>82</sup> In addition to the oxides of lanthanum and thorium, substitutions of lithium, beryllium, calcium, and boron were made.

A description of the method of optical glass manufacture as practised at the U.S. Bureau of Standards has been given by F. W. Glaze and C. H. Hahner,<sup>83</sup> and a review of developments in optical glass which have taken place in England over the past century has been given by W. H. S. Chance.<sup>84</sup>

### Miscellaneous

During the year, several important papers have been published which cannot properly be included under the main headings of this review.

W. A. Weyl<sup>85</sup> has discussed some practical aspects of the surface chemistry of glass with reference in particular to the chemical processes involved in the reactions between cleaning solutions and the glass surface. While in contact with acids, films are formed on the surface, while alkalis break down the silicon-oxygen structure. The rate of attack by alkali is reduced considerably when beryllium or aluminium ions are present in the glass.

In a paper on the physics of adhesion N. A. de Bruyne<sup>86</sup> has discussed the molecular forces and the strains at the interface between adhesive and adherents. The sealing of glasses to metals is a particular case and this is discussed in some detail with reference to the effect of oxidation of the metal.

The applications of nuclear physics to the ceramic industries have been surveyed by J. R. Johnson.<sup>87</sup> After outlining the recent developments on the theories of fundamental particles and forces, the emission of radiation and the relationship between mass and energy, Johnson discusses the possible uses of radioactive isotopes as tracers in ceramic research, for example, for studying the rate of diffusion of sodium ions into glass at various temperatures.

A novel method for investigating the history of glass surfaces has been described by J. F. Dreyer and C. W. Ertel.<sup>88</sup> A light polarising solution known as "Polacoat" when applied to a glass surface and allowed

to dry is found to be sensitive to the orientation of the surface. For the purposes of observation, the dry film is stripped from the surface and examined under an analyser. It is claimed that there are marked differences between films taken from an abraded surface and a polished surface, and it is evident that the material will have some useful applications in the glassworks laboratory.

A detailed account of the pyrometric methods available to the ceramic industries has been given by V. L. Parsegian.<sup>89</sup> The review includes thermo-electric, resistance, optical, and radiation pyrometry, photo-electric cells, and automatic temperature control, and there is an extensive list of references to the literature of the subject.

A general survey of recent progress in the physics of glass has been given by H. Moore,<sup>90</sup> and A. Silverman<sup>91</sup> has described recent developments in glass manufacture in the United States.

As with many other industries, the glass industry has accumulated a large number of technical terms peculiar to itself and a committee of the American Ceramic Society has done a valuable service in compiling a glossary of terms which was published during the year.<sup>92</sup>

The family of substances known as the silicones have many properties in common with glasses and for this reason can usefully be included in this review. In a general article on the subject, H. J. Emeléus<sup>93</sup> has described the method of production, their properties, and applications. The silicones find important uses in their application to glass surfaces, and a detailed investigation of the properties of poly organosiloxane surfaces on glass has been carried out by M. J. Hunter *et al.*<sup>94</sup> A variety of films was used and the angle of contact with water, the surface resistivity and the dry lubricity of the treated surfaces were found to increase considerably over the values for untreated glass. The development of surface properties was attributed to the formation of a chemical bond between the surface film and the glass. The subject has also been studied by D. O. Richards and L. A. Spitze,<sup>95</sup> who examined the water-repellent nature of glass surfaces treated with different silicones by contact angle measurements. Results are given showing the effect of various silicones, types of glass, temperatures, and duration of heat-treatment and surface roughness on the contact angles. It was found that the maximum water-repelling power was obtained with silicones containing dodecyl and octadecyl groups and glasses rich in alkali gave the highest contact angles.

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# CERAMICS, REFRACTORIES AND CEMENTS

By S. W. RATCLIFFE

**D**EVELOPMENT in the pottery industry of this country is centred round its mechanisation, modernisation, and rebuilding. Most manufacturers of earthenware are replacing their hand machines with semi-automatic machines, which has resulted in an increase in production, but not at the expense of quality. The general policy appears to be the production of high-class, medium-priced ware. The use of automatic machines for making necessitates a greater degree of control over the consistency of the clay body from which the ware is made, particularly moisture content, shrinkage, and plasticity. There also appears a tendency for greater discrimination in the choice of raw material, partly due to the use of automatic machines, and partly to a greater appreciation of the technical control for specific purposes. In the bone china industry the development of automatic making has been restricted because of the lack of plasticity in the body, but such a body could be improved by the addition of a plasticiser, which would make the use of such machines a possibility. Very little change in body composition has been made over a long period in certain sections of the industry, but with the advent of greater mechanisation and the possibility of quicker firing schedules for increased production, new bodies may have to be developed. The industry is alive to all these possibilities.

The porcelain industry is interested greatly in the special ceramics, containing  $\text{BeO}$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$ , etc., and a plea is made<sup>1</sup> for the development of entirely new composition and techniques in the industry to keep pace with developments in nucleonics, radar and in jet engine and rocket propulsion.

Tunnel ovens for all classes of pottery are in great demand. In the usual type of tunnel oven the transfer trucks, which carry the ware through the oven, have a base of thick refractory and insulating material. The cross-section of this type of kiln varies, but is approximately 3 to 4 ft. Some interest is being taken in a kiln, consisting of a number of small chambers<sup>2</sup> varying in cross-section depending on the goods to be fired. No trucks are necessary: the goods are pushed through on bats. With this type of kiln the throughput may be increased and some interesting developments may arise. Most of the tunnel-ovens are fired either by gas or electricity. There is some concern because of the present uncertainty of the fuel situation. Gas supplies are limited and, on the other hand, it is not known whether by installation of electric kilns the power to meet the greatly increased demand would be available. With electrically-fired kilns and with increasing demand for electrical power for operating all types of equipment in other processes, any interruption or breakdown in electrical supplies will have the most serious consequences.

In the refractory field, with the use of oxygen to attain higher temperatures, interest is concentrated chiefly on refractories for higher temperature work. For this reason interest is shown in sintered refractories. It is

still too early to say whether such refractories will be economic for use in large furnaces, or whether their use will be limited to special equipment only. Much interest is still concentrated on the all basic lining for steel manufacture, and the behaviour of such linings under the conditions of steel production is now reported.

The general development in the iron enamelling industry is one of mechanisation. Before the war, only a few of the manufacturers operated with conveyor equipment; to-day it is common. The pickling room, in which the metal is treated before its subsequent enamelling, was always an unpleasant department, oppressed with steam and acid fumes. A suggested type of apparatus to replace all this is the so-called spray pickling machine,<sup>3</sup> in which the ware is carried through a closed tunnel and sprayed with the various solutions in normal sequence. Such a machine, fully enclosed, offers advantages, such as greater facility in filtering and cleaning of the solutions. At the moment, it is rather early to compare the cost per sq. ft. of ware passing through with that of any other method, because there are insufficient machines of this type in service.

With regard to the enamel composition, there appears to be a trend for lower temperature enamels, decreased coat thickness, and increased acid resistance.

### Clays and other raw materials

The clay-water relationship has interested investigators over a long period. It is quite understandable, for the clay-water structure is of fundamental significance in the preparation of clay ware. No other finely divided material when mixed with water shows the phenomenon of plasticity, except to a negligible degree. Macey has suggested that some idea of plasticity can be formed from the phenomenon of backlash and also from the elongation of a bar of plastic clay. It is doubtful whether either of these afford a measure of plasticity. Backlash is a phenomenon first reported by Macey in 1941 and it again appears in the literature under review.<sup>4</sup> It is difficult to describe but very readily recognised by feel. If a portion of the clay be held in the thumb and finger of both hands and alternately pulled and compressed, a looseness is felt. There is a range of easy movement, culminating in each direction in a sudden resistance. The sensation is reminiscent of play in a joint or the behaviour of a nut on a worn thread, from which analogy is suggested the name backlash. Macey found backlash present in short sandy clays, but not in highly plastic materials. Williamson<sup>5</sup> observed it in ball clays, but agrees that it is more noticeable in less plastic materials. The phenomenon is not apparent in a freshly moulded piece of clay, but develops after alternate compression and extension. It is suggested that the particles have been arranged in a new packing. Whether backlash can be explained merely by differences in packing or whether there is some connection between thixotropy and backlash is not yet clear. At the moment this property of backlash is only a matter of interest. There does not appear to be any direct connection with the making processes, for none of them actuate by alternately pulling and compressing, except perhaps the operation known as "wedging."

The idea of the extension of a clay bar when subjected to a tensional force to indicate plasticity, is old. Macey<sup>6</sup> suggests that the "local elongation" should be measured for the purpose of indicating plasticity. "Local elongation" refers to the clay pulling out into a "neck" after the maximum observed stress is reached or has been passed. The author points out that serious discrepancies occur in the results and this method therefore cannot as yet be accepted for plasticity measurement.

The silica stone used for the manufacture of silica bricks contains at least 97% silica; of the other constituents these should be less than 1.0% alumina, less than 0.3% alkalis, and very little lime. Expressed in mineralogical composition, the material should be composed wholly of quartz. If constitution was the only criterion, the quantity of material available would cause little concern, but to produce silica bricks, certain physical properties are necessary. The rock must crush and give a certain grading. The rock which crushes into a coarse fraction (say 5 mm. or more across) and fine particles (say less than 0.01 mm. across) with few particles of intermediate size is regarded as ideal. A further consideration is the porosity of the stone after firing; this should be as low as possible. The behaviour on firing is also important. The material when formed into shapes should invert to the low specific gravity form without shattering. At present the specification eliminates vein-quartz as a source of raw material, for although it is often sufficiently pure and compact, the individual quartz crystals contain innumerable minute bubbles, like inclusions of air, which increase the tendency to shatter on firing. Ganister and silica rocks are the materials usually used. Rocks containing a high proportion of metamorphic quartz grains invert more quickly and more thoroughly than those rich in igneous quartz grains. The sources of rock in the British Isles, useful for the manufacture of silica bricks have been reviewed,<sup>7</sup> and it is pointed out that quartzite of the quality most desired by silica brick manufacturers nowadays has an extremely limited distribution in Britain. Research is necessary on the use of different quartzitic materials for this purpose. Extensive deposits of massive crypto-crystalline chert are found in America,<sup>8</sup> and are used for the production of silica bricks. It is stated that the results show that suitably processed, the crypto-crystalline chert gives a refractory similar to commercial silica bricks from quartzitic ganister. The use of crypto-crystalline quartz (flint) for the production of silica bricks was tried many years ago in this country but the bricks were not up to the usual standard.

Bentonite is used in glazes to improve suspension and in bodies to improve plasticity and strength.<sup>9</sup> A critical review of the classification and testing of bentonites has been made.<sup>10</sup> The amount of minerals of the montmorillonite group present in the material is not a complete criterion of its properties; the particle shape and size also influence the properties. Fractions of both American and German bentonite have been examined by means of the electron-microscope.<sup>11</sup> The particles of the German bentonite were rough and badly shaped, and likely to bind closely together, whilst those of the American bentonite were smooth and well formed and likely to form films very readily. It is suggested that these characteristics probably explain why the German bentonite

swells very rapidly and gives greater green strength to ceramic bodies, while the American is more suitable for making thin films.

The effect of particle shape and grain size distribution of talcs on the properties of casting and pressing of articles is published<sup>12</sup> by W. W. Gaskins, but he has not disclosed any new facts of general importance to the industry. He found that the finer the talc in grain-size (as determined by specific surface measurements) the higher the viscosity of the slip for a given specific gravity or pint weight. This change in viscosity with fineness of grinding is well known in the pottery industry where this property of viscosity is of some importance in glaze preparation. Not only is viscosity influenced by grain size but also by the soluble salt content. The viscosity changes with the amount of deflocculents or flocculents present. As a measure of control in glaze dipping, it is not unusual to add some flocculent to adjust the viscosity to the required figure. With regard to the pressing of bodies, the above author states that those containing talc of low specific surface give bodies with a less tendency to laminate than talcs of high specific surface. Here particle shape may play a big part.

Silicon carbide is usually bluish black in appearance. A description is given<sup>13</sup> of a synthetic colourless silicon carbide, which has gem properties superior to those of the diamond. Some compositions and details of manufacture of synthetic gems is also given.<sup>14</sup>

The actual mechanism of the decomposition of kaolin and the subsequent formation of mullite is a fascinating subject, but it cannot yet be assumed that the exact mechanism has been established. The method of thermal analysis of kaolin and the characteristic thermal curve have been examined by many investigators. Two salient features of the curve are immediately apparent. At approximately 500° to 600° c. the hydroxyl groups, which are present in the kaolinite structure, are combined to form water and expelled from the crystal with absorption of energy and loss of weight. This is not completely reversible, only minor amounts being regained upon cooling. The other feature of the curve is the sudden exothermic reaction at about 980° c. which indicates a crystallisation process. On further heating there appears to be no doubt that mullite is gradually formed. The problem is to decide whether after the decomposition at about 600° c. the alumina and silica are present merely as a mechanical mixture and the sudden exothermic reaction at about 980° c. is due to  $\gamma$ - $\text{Al}_2\text{O}_3$  or if there is some other explanation. J. E. Comeford, R. B. Fischer, and W. F. Bradley,<sup>15</sup> by means of X-ray diffraction diagrams and the electron-microscope studied the material after heating to a series of temperatures, but found no direct evidence to show the exact nature of the regrouping after the loss of water. However, they believe that  $\gamma$ - $\text{Al}_2\text{O}_3$  was not a factor in the mechanism and that the exothermic peak shown on the graph of the thermal analysis curve is explained by the energy which accompanies the integration into crystal mullite. M. Kantzer<sup>16</sup> confesses that an X-ray diffraction examination of the effect of heat on kaolin has not been very helpful in clarifying existing conflicting ideas on the structural changes associated with the thermal changes occurring between 100° and 1220° c.

### Ceramic bodies and making processes

Electrical porcelains are now being manufactured for extremely diverse purposes in the electrical industry, the demands of which range from low to high voltage and frequency. The potentialities of steatite, rutile, titanite, mullite, and zircon porcelains are realised.<sup>17</sup> The latest bodies consist of sintered oxides of alumina, beryllia, zirconia, and thoria yielding crystal systems at elevated temperatures. The common method to give strength to a ceramic body is to form a glass bond, although the idea of sintering and crystal formation to develop strength is not new. Porcelains which show exceptional mechanical strength and dielectric strength at temperatures up to 1100° c. have been developed. These are all of the crystalline type using alumina, beryllia, zirconia, thoria, with small additions of other metallic oxides and no silica.<sup>18</sup> These glass free ceramics have proved highly resistant to creep or deformation at temperatures up to 900° c. for long periods of time. These materials have a high thermal conductivity which is in the order of from four to ten times that of pure alumina compositions.<sup>19</sup> The conditions for sintering of refractory oxides is discussed by R. Lecuir.<sup>20</sup> The refractory oxides will have a gaseous layer adsorbed on the surface of the grains, which can be replaced by a molten organic solid such as urea. A forming pressure of two tons per sq. cm. will then produce a mechanically strong agglomerate from which the organic binder can be eliminated by slow heating (75° to 100° c. per hour) without diminishing the intimacy of contact between the particles. Continued heating at higher temperatures causes a sintering by recrystallisation alone. The state of the original material influences the porosity of the finished mass. The particles should not be initially too crystalline. Electrically fused magnesia, which is markedly crystalline, gives a density of 2.2 when heated to 1500° c., whereas agglomerates of pure magnesia similarly treated give a density of 3.29. An agglomerate of anatase may be sintered to a non-porous mass of rutile at 1220° c., but in the case of alumina and zirconia large increases of volume occur on heating and a non-porous mass cannot be attained at temperatures below the melting point. J. M. Revels<sup>21</sup> draws attention to the fact that the sintering temperature alters the shape of the interstices and in the case of titania, because of this variation in shape, the permittivity varies with the sintering temperature. The published work on sintering draws particular attention to the shape and grain size of the original material. If the raw material must not be too crystalline, it seems obvious that by grinding the material to an ultra-fine state, better control of sintering would be possible. The use of high pressures in making also may help in this direction. It may even be possible to sinter by induction heating, which if successful would make the problem much easier. One can visualise the material being moulded, and then sintered by induction heating before being released from the mould. It is possible that such a method may well present a problem in finding suitable material for such moulds.

Alkaline earth titanates still attract attention in the field of research. Previous work on barium strontium titanates indicated the usefulness of these materials for capacitors. The barium magnesia titania series have shown rather variable results. Some investigators produced

porcelains of high electric losses and others of low electric losses. The latter series have been further investigated,<sup>22</sup> and it is shown that these porcelains change their properties with time. It appears<sup>23</sup> that all alkaline earth titanates change their dielectric constant value over a wide range with slight change in temperature or composition, and this probably explains why these bodies are still in the experimental stage.

Investigations into the problem of vitrified compositions of high thermal shock resistance have proved fruitful. The thermal shock resistance of steatite has been increased by the introduction of zircon.<sup>24</sup> The best way in accomplishing this is by the use of barium zirconium silicate. The electrical and most of the physical properties are said to be unaffected except the coefficient of expansion, which is markedly lowered.

For the purpose of preventing adsorption and condensation of water on the surface of glass and steatite ceramic substances, the articles can be treated with quaternary ammonium compounds.<sup>25</sup>

Metal layers can be applied to ceramic surfaces by a spraying process, by cathode-volatilisation, etc. In all these methods, however, no interaction takes place between the metal and the ceramic, and consequently the metal coating does not adhere firmly to the surface. For the coating of ceramics, a mixture of iron and/or nickel powder with copper powder is applied to the article with a finely ground ceramic flux.<sup>26</sup> It is necessary to fire the coated article in a reducing or neutral atmosphere. Such ceramics are readily wetted by silver solder.

Drying methods for clay-ware have been the subject of a good deal of attention during the last few years. This is readily understood because with increased production from the semi-automatic machines, quicker drying times than of old are essential to prevent a bottleneck in production. No particular new developments appear in the literature under review. Humidity drying,<sup>27</sup> infra-red drying,<sup>28</sup> and hot floor drying for heavy clay-ware<sup>29</sup> are all discussed. A British patent<sup>30</sup> appears, in which the contour of the heating elements correspond to the outline of the piece to be dried. This presumably, is to overcome the difficulty of shadow effect experienced in radiant dryers. An interesting paper on the vapour pressure/moisture content/temperature relationship appears.<sup>31</sup> Isotherms were constructed from the clays studied and are of the usual hyperbolic form. It is common knowledge that when clays containing moisture are heated on one side, moisture moves to the cooler side. Most industrial drying processes make use of heat to accelerate the drying rate and appreciable temperature gradients are likely to be set up within the ware. The authors are concerned with the second stage of drying, *i.e.*, in the leather hard state, when shrinkage has practically ceased. It is suggested that when large articles in the leather hard state are placed on a hot-floor dryer, steep moisture gradients are produced with consequent proneness to trouble.

Methods of dry mixing of bodies are increasingly being used, particularly in America. There are many advantages of dry mixing, such as less labour, less plant and less power required. Recent advances in mixing procedures are given by R. Wiegel.<sup>32</sup> In the pottery industry the term dry mixing is given to the preparation of bodies in which the raw materials are measured dry and afterwards mixed with water in a blunger in order

to break down the lumps, and to obtain intimate mixing. After this preliminary process the slip is cleaned by passing over lawns and magnets, and subsequently filter pressed to obtain the plastic body. In the dry method of mixing, as used in the United States<sup>33</sup> and elsewhere, the raw materials are mixed dry and then sufficient water is added to give the necessary workability to the body. English potters still prefer the slip method of preparation, because it is possible to lawn and magnet the body to eliminate coarse material such as sand and lignite, also materials which affect the colour. Previous work has shown that the dry method of mixing does not give the same intimacy of mixing that is obtained by slip mixing. The lack of intimate mixing is reflected in the quality of the ware.

A development in the porcelain field is the semi-conducting porcelains. Porcelains of this type are produced by the addition of certain metallic oxides, and the resistivity of the porcelain can be varied within certain limits.<sup>34</sup> These porcelains are characterised by high temperature coefficients of resistance. Other types, which are composed of a mixture of silicon carbide and a ceramic bond fired in a reducing atmosphere have a resistance which varies with voltage. Certain types of the silicon carbide semi-conducting porcelain are used in micro-wave measurements and in radar equipment to avoid unintentional broadcasting of signals. A patent on semi-conducting porcelains is also published<sup>35</sup> in the literature.

### Glazes and colours

The regulations prohibiting the use of raw lead-glazes will soon be enforced. These regulations not only cover raw lead-glazes, but all glazes which contain lead in a form dangerous to health. The glaze is looked upon as being dangerous if the percentage of lead oxide dissolved is 5% or over when treated with mineral acid of a specified strength. The solubility is determined by shaking half a gram of the ground material with 0.25% hydrochloric acid for one hour and determining the lead oxide in the solution. Glazes which contain lead in a low solubility form have been used for some time by most earthenware manufacturers, and only tile manufacturers have used glazes containing lead in a highly soluble form. The reason for this is that certain decorative effects are produced more easily in such a glaze. Low solubility glazes are made from a lead frit, specially prepared to give a low solubility. This frit is made by fritting (fusing) the lead compound (usually red lead) with silica in definite proportions to produce lead bisilicate. This silicate has a low solubility figure. By using such a frit, the percentage of lead is restricted by the ratio of lead to silica. If it were possible to produce a lead frit of high lead to silica ratio and still obtain low solubility, tile manufacturers could still produce similar decorative effects to those in the raw glaze. A process, for coating ground materials of any composition with a layer of insoluble material, is described.<sup>36</sup>

In the case of a lead frit, the frit is ground and a stabilised silica ester is added in a suitable solvent. On drying out the ester polymerises, leaving each particle of frit coated with a thin film. This film which is impervious to, and insoluble in, dilute acids, consists essentially of silica

and the chemical properties are not affected by the coating material. Such a frit should always be within the prescribed limits of solubility. Unfortunately, this frit is only a part of the glaze and it is necessary to mix at least a borax frit and china clay with the lead frit. This process is usually performed in a mill where further grinding and mixing occur. Further grinding of the coated frit increases the lead solubility and the advantage gained by coating is gradually lost. Probably some other method of the preparation of the glaze can be devised, to obviate the necessity of grinding. No evidence of the effect of a coated high solubility frit on the human body is yet available. The idea is excellent and probably we shall hear more about the process.

A stain ranging in shade from ivory to yellow can be obtained by mixing pure zirconium oxide with ammonium metavanadate and firing to a temperature about  $1400^{\circ}\text{C}$ .<sup>37</sup> The product should be finely ground. Colours ranging from blue to blue-green are also claimed which consist of oxides of silicon, zirconium, and vanadium:  $\text{ZrO}_2$  35–80%,  $\text{SiO}_2$  55–10%,  $\text{V}_2\text{O}_5$  3–17%.  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , or  $\text{Li}_2\text{O}$  is present in proportions molecularly equivalent to 0.5.<sup>38</sup>

Crazing in the pottery industry is a definite and serious fault, and not a decoration, although it is used as a decoration for certain types of ware; the so-called "crackled" ware. Crazing of the glaze is due normally to the low firing of the biscuit ware or to the fact that the body does not suit the glaze. Fortunately, the crazing of glazes does not present a great problem in the pottery industry to-day. The practical methods of maintaining a craze free glaze over a reasonable time period are well known, but there are many problems in connection with crazing which attract the research worker. Much of the crazing which is experienced at the present time is delayed crazing, i.e., crazing which occurs after storing. There should be no signs of immediate crazing from the glost oven. To resist crazing<sup>39</sup> P. E. Cox suggests that in general the silica content of the fired body should be about 73–75% and for highly alkaline glaze the silica content should be higher. The silica content of the body is a good means of control, but it is not true to say that such a body will not craze. The normal earthenware body of the English type is porous and it is necessary to put the glaze in compression by using a body of higher thermal contraction than the glaze. To obtain this higher thermal contraction over the proper range of cooling, the body must be fired to a sufficiently high temperature to convert some of the free silica in the body to cristobalite which has a high thermal contraction at about  $225^{\circ}\text{C}$ . A body with the correct silica content if fired at a low temperature will not produce the necessary compression in the glaze.

As previously mentioned, crazing is more a problem of delayed crazing. This problem of delayed crazing has attracted attention for some years, and one of the suggested reasons was the after-contraction of the glaze. Examination of ceramic ware in use or in storage, shows that the stress in the glaze developed during the cooling in the glost-oven, does not remain constant during ageing, but that the glaze compression decreases and tension often arises causing delayed crazing of the glaze.<sup>40</sup> It is well known in thermometry that the freezing-point marked on the glass thermometers varies with time. Glass previously heated does not

complete its thermal contraction when cooled but shows an after-contraction for several months. A glaze is very similar to glass and it was believed that this delayed thermal-contraction was the chief cause of delayed crazing. In 1928, Schurect showed that the moisture of the air is adsorbed by the ceramic bodies and expands them. This expansion of the body will also help to decrease the compression stress in the glaze. The moisture expansion of the body and the after-contraction of the glaze have been considered to be somewhat equal possible sources of delayed crazing. L. Mattyasvosky-Zsolnay placed glazed ware in a perfectly dry and humid atmosphere for a reasonable time exposure. He then tested the compression in the glaze and found that only when the body adsorbed moisture did the glaze-compression decrease. The effect of the after-contraction of the glaze was not measurable. He concludes that delayed crazing arises not from the after-contraction of the glaze, but more probably from moisture-expansion of the body. Moisture is adsorbed by the biscuit ware over a number of years, causing a slight expansion of the body. A similar expansion can be created by steam in an autoclave during a much shorter period and this fact is taken into account in testing the resistance to crazing of ware. It is usual to place the articles in an autoclave and subject them to steam pressure. L. Mattyasvosky-Zsolnay (*loc. cit.*) suggests that if glazed wall tiles are subjected to a steam pressure of 100 lb. per sq. in. for two hours in an autoclave and show no signs of crazing the tiles can be guaranteed for 20 years of service under normal conditions. The same steam pressure and time cannot be used for all types of ware to give the same guarantee of resistance to crazing. For sanitary ware steam at 150 lb. per sq. in. for two hours should give 20 years of service under normal conditions.

## Enamels

In the process of porcelain enamelling the first operation and one of great importance is the preparation of the metal for subsequent application of the enamel, either by dipping or spraying. This metal preparation is accomplished by first cleaning the metal, followed by acid-pickling for the removal of rust and scale, plus various subsequent stages such as neutralising, etc. Most manufacturers are using the bath method immersion by use of hoist or special conveyors. With the advent of spray cleaning and pickling<sup>41</sup> this process will be changed. An horizontal tunnel is usually used, and the ware is carried in baskets by an ordinary monorail conveyor. As the baskets are conveyed through the tunnel the various solutions are sprayed on to the ware. The solution at each stage is re-circulated by a pump. All solutions are kept automatically at a predetermined constant temperature. Where a final nickel flash is given, the nickel tank is equipped with a  $p_H$  recorder and filter equipment. It is claimed that much time is saved by this method and that the human factor is eliminated to a large extent. There has been some doubt about the proper nickel deposit from sprayed solutions but it is not considered that the deposit of nickel on sprayed ware is as uniform as by dipping. Bright annealing is another method suggested for metal-finishing. This method consists of heating the metal parts in a controlled atmosphere,<sup>42</sup>

when the iron oxide on the metal surface is reduced to the metal. The gas may be obtained by cracking ammonia and contains 11 to 20% of hydrogen and 89 to 80% of nitrogen.<sup>43</sup> Many advantages are claimed, including speed of production, cleanliness and the reduction of labour. Against this is the cost of equipment, which may be offset by cheaper production, but one very serious drawback to this type of cleaning would be warpage of the metal.

Of interest to the enameller is the de-enamelling of enamelled sheet<sup>44</sup> which have been rejected for enamelling defects. Processes which have been used for this purpose are sand blasting or chemical methods. The chemical methods which have been tried are treatment with hydrochloric acid, sulphuric acid, chromic acid, hydrofluoric acid, sodium hydroxide solution, and fused sodium hydroxide. That most used at the present time is the sodium hydroxide solution. Most methods possess serious drawbacks such as liability to attack the under-lying metal. A suggestion is made that the porcelain enamel can be removed from steel by a 30-minute immersion in hot hydrochloric acid containing 4 oz. per gallon of fluorspar.<sup>44</sup> Complete cleaning of the residue left by chemical solution is accomplished by sand-blasting. The process of sand-blasting is not always suitable for thin sheet steel on account of the distortion which it can cause. A. Kelly<sup>45</sup> prefers the molten sodium hydroxide method, which is probably the fastest, but safety hazards are involved.

In the preparation of enamels by the wet-process, clay is looked upon as being almost essential in order to prevent setting.<sup>46</sup> The selection of the clay is an important consideration, as the impurities in the clay may lead to pitting or scumming. Other properties such as reflectance, colour, gloss, and acid resistance of fired enamels depend upon the clay used in the mill addition.<sup>47</sup> The clay imparts strength to the dry enamel and the inorganic salts used as setting-up agents will have a definite effect on the character of the enamel film. Occasionally gum tragacanth or gum arabic is used to give the desired strength. A suggestion that urea might be a useful addition is made,<sup>48</sup> but it should be used with caution.

The literature for the period under review is partly concerned with the effect of titania in enamels as an opacifier. W. J. Baldwin<sup>49</sup> states that enamels of good opacity can be produced with low silica-content (10–20%). These enamels contain  $P_2O_5$  and  $Al_2O_3$  as essential constituents. By adjusting the percentages of  $SiO_2$ ,  $Al_2O_3$ , and  $P_2O_5$  the amount of titania to give optimum opacity can be reduced considerably. The use of zirconia in such enamels is a definite advantage. Another type of enamel, a one-coat finish<sup>50</sup> which is probably the goal of the porcelain enamellist, is also characterised by low silica content but with little or no alumina.<sup>51</sup> High barium oxide content is desirable and molybdic oxide seems to be a good ingredient to promote adherence. Titania enamels can vary in colour. The yellow tint was at one time attributed to iron oxide, but addition of as much as 0.5%  $Fe_2O_3$  and 0.2%  $V_2O_5$  to the enamel did not cause any appreciable variation in colour. Chromic oxide although only present in small amounts appears to be the real culprit.<sup>52</sup> Another change of colour which is of interest is the change with firing treatment from

bluish-white to a cream-white. The fired enamel consists essentially of opacifying particles with a refractive index different from that of the clear glass matrix. The opacifying particles will consist of rutile and anatase. The anatase crystals are small and tend to be spherical, whereas the rutile crystals are present as irregularly shaped particles. Small opacifying particles cause a blue colour to be reflected from the fired enamel. This phenomenon of blue colour of a medium containing small dispersed particles in suspension, was noticed by Tyndall 80 years ago. When anatase crystals are present, the small particles scatter the light to give a bluish-white appearance. When the temperature is raised from say  $815^{\circ}$  to  $870^{\circ}$  C. the amount of anatase falls and the amount of rutile increases.<sup>53</sup> This appears to be more affected by firing temperature than by changes in firing time. The change from bluish-white to cream-white with temperatures of firing is attributed to the change in crystal form, which causes a difference in the scattering of the light. In the use of titanium enamels the surface of the metal must be treated with extra care. Thin application is the prime advantage of titanium enamels. Old opaque enamels had coatings of 0.012–0.014 in. thick. The zirconia opacified enamels had coatings 0.009–0.011 in. and the titanium enamels 0.005–0.007 in. with a firing temperature of 35 to  $55^{\circ}$  lower.<sup>54</sup> But these thin coats require blemish-free steel and ground coat.<sup>55</sup>

It is suggested by E. E. Bryant and M. G. Ammon<sup>56</sup> that the thermal-expansion data on frits is not alone sufficient to give exact indications of the stresses which will be set up in the enamel when applied as a coating. This conclusion is in harmony with the findings of other investigators.<sup>57</sup> There are many physical properties which are difficult or impossible to measure. Many of these properties could have an effect on the fit of the enamel coating. It is possible that there could be a skin effect on the enamel, which might produce stress during cooling. The normal firing of the enamel may not produce complete fusion and any crystalline phases present may affect the fit of the enamel. The difference in the rate of cooling of the iron and enamel leads to a temperature difference which again may affect the fit.

Lithium compounds are accepted as materials to be used in many ground coat enamels, particularly in America. Lithium manganite has been used in a number of plants.<sup>58</sup> The use of lithium compounds in cover coats is more recent and hence less information is available. For the most part the use has been limited to titania opacified enamels. Titania enamels containing 1–1.5% lithium silicate are in use. Firing temperature and speed of travel of goods through the furnace vary from plant to plant, making it difficult to correlate the effect of lithium silicate on the titania-opacified enamels. Generally, lower temperature and shorter firing times have been effected. The lithium silicate could not be used as a mill addition. Both lithium titanate and lithium zirconate have been substituted for some of the titania in cover coats with marked improvement. Work on these compounds is quite new and not too widespread, but results have been promising.

A method of decorating similar to the silk screen process is suggested.<sup>59</sup> The pattern or design is held magnetically to the surface of the sheet

during the spraying process. A magnetic-table is used which accommodates a wide range of sheet sizes. The underside of the pattern is metalised with iron to enable it to be held by the magnetic-table. The idea has obvious limitations, but there are probably a number of designs which would lend themselves to this type of work.

A very interesting innovation is the use of porcelain enamels as "wall paper." This is prepared by firing thin sheets to 500° c. The total thickness of the coat sheet, which is applied to walls with linoleum glue, is 0.022 in.<sup>60</sup>

Results of investigation of common defects produced in manufacture are published. Scumming due to sulphur gases and incorrect firing<sup>61</sup> and the causes of blistering<sup>62</sup> are discussed.

## Refractories

"Grog" is a material used in the manufacture of refractories made with clay, which type of refractory is in good demand for the lining of the lower temperature furnaces such as boilers, potters ovens, firebacks, saggars, and certain metallurgical furnaces. This mixture of clay to grog varies, but is in the order of 50 to 70% of clay. The "grog" consists of small particles of non-plastic refractory materials and may be either small fragments of refractory clay material which has been burnt at a high temperature, or some other non-plastic material such as mullite, sillimanite, etc. Without the addition of "grog" it would be impossible to shape, dry and fire commercial wares because of the excessive stickiness, high shrinkage, and the tendency to crack. Such properties as stability under load, and spalling properties are influenced by the "grog" addition. In fire-brick manufacture it has been generally accepted that sharp angular particles are required, because a greater binding strength is obtained by such "grog." It is now reported that angular particles influence the spalling resistance adversely. According to W. F. Ford and W. J. Rees<sup>63</sup> the spalling resistance of magnesite products is reduced the more angular the material, due to higher porosities and to tendency towards friability. This may be a special case where angular particles are a disadvantage. There still appears some doubt about the temperature of firing clay to produce "grog" for fire-bricks. The question is, should the clay to produce the "grog" be fired at a low temperature of say 500° to 800° c. or should it be fired at a higher temperature of say approximately 1400° c.? V. A. Rybnikov<sup>64</sup> disputes the claims made by earlier authors regarding the advantages of low-fired "grog." In particular refractories based on low-fired "grog" are said to be difficult to dry and to have poor resistance to spalling, in addition to the various disadvantages associated with the large firing shrinkage. On the other hand, R. R. Bowman and R. B. Burdick<sup>65</sup> found some advantages by using low-fired "grog" in the preparation of soft mud bricks.

Future progress in iron and steel furnace technique will depend greatly upon whether refractories can be produced capable of withstanding higher temperatures and more exacting conditions than those now being manufactured. Oxygen is being used as an addition to the air mixture, both in the steel industry<sup>66</sup> and the iron industry.<sup>67</sup> The addition of oxygen to the air in the melting of steel in open-hearth furnaces causes

higher flame temperatures, which might adversely affect the refractories. J. J. Golden<sup>68</sup> came to no definite conclusions on the effect of oxygen in open hearth furnaces on the life of the furnace lining, owing to the fact that the oxygen was used only intermittently. On the other hand, G. V. Slottman<sup>69</sup> mentions that no difficulty with excessive roof wear was experienced and suggests that the cost of roof-refractories per ton of steel will actually be lower than normal. The major difficulty reported appears to involve excessive slag accumulation on the walls of the down-takes and more rapid fouling of the checkers. Tests are still proceeding on basic refractories and oxygen in open-hearth furnaces.<sup>70</sup> Although these opinions suggest that the refractory materials now being used are of sufficient refractoriness, developments are in progress to enable furnaces to withstand higher temperatures.<sup>71</sup> Clay was used at one time as a binder but it is now recognised that refractory bricks capable of withstanding higher temperatures are obtained by reducing the clay addition to a minimum, making use of a temporary binder. The bonding agents may be inorganic or organic.<sup>72</sup> Among the organic bonding agents are dextrin, casein, glue, and resins. Although at present there are few applications of synthetic plastics in pure refractory production, the possibility of their use is discussed by H. M. Glass.<sup>73</sup> Of the resins of actual or potential use are the urea- and phenol-formaldehydes, derivatives of furan, polyvinyl alcohol, and the silicones and silicon esters.

Most refractories, in fact, most ceramic articles, consist of a crystalline phase set in a glassy matrix. Up to fairly recently, it was considered most essential that fluxing of some description was necessary to give strength. During the past few years information has become available on the properties of sintered oxide refractories. The mechanism of producing this kind of refractory, as mentioned earlier in this report, is that certain oxide powders sinter, if exposed to temperatures lower than the melting point. For instance, at 1650° to 1700° c. alumina will sinter and will undergo about 40% reduction in volume.<sup>74</sup> At the same time the original crystals grow to at least ten times their original size.<sup>75</sup> Sintering depends on a greater energy of the small particles surface, and when the process is finished the crystals lose their identity and grow into one another. It implies that there is a certain vapour pressure at sintering temperatures. For alumina, the actual value is a few millimetres of mercury at 1700° c., rising to 200 millimetres at 2100° c. This vapour pressure is probably responsible for some of the weight loss which is always observed during sintering.<sup>76</sup> The properties of some of the sintered materials are remarkable. For instance, the tensile strength of sintered alumina at 1200° c. is only about 15% lower than at ordinary room temperature. At the moment one of the principal obstacles to the more extended use of sintered oxide refractories is the inconsistency of their mechanical properties. Long firing times will lead to the development of very large crystals and it has been shown by A. L. Robert (*loc. cit.*) that a coarse grain leads to brittleness. Gas bubbles may influence the properties. These are a source of weakness and are probably derived from gas originally trapped. One of the outstanding properties of sintered oxide products is their low porosity. No voids remain open to the surface. The melting of metals has been one of the earliest applications—thoria and beryllia

pots for melting metals. Both sintered alumina and beryllia have a high thermal conductivity and may have many extended uses. Whether or not sintered oxides can be used at high temperatures is not yet clear. It might be thought that the absence of the glassy bond will largely prevent subsidence, but there is a possibility that recrystallisation under stress might occur causing flow.

A high refractoriness, though of prime importance, is not the only requirement for a refractory material. The action to slag attack is also important. In this respect zirconia refractories, which are not of the sintered oxide type, but made from zircon minerals, are very resistant to attack by certain types of slags, but suffer from the disadvantage that zirconia inverts at about  $1000^{\circ}\text{C}$ ., and the refractories have not a good spalling resistance. The thermal shock resistance can be improved by diminishing or eliminating the thermal-expansion which occurs during inversion. The thermal-expansion can be diminished to give a material of good thermal shock resistance by the addition of lime or lime and magnesia.<sup>77</sup>

In the pottery industry in this country, it has been the aim to produce light kiln furniture and so increase the loading space for ware as much as possible, but in the United States, the production of light kiln-furniture has not progressed so much as here, possibly because the fuel supply is not so serious a factor. Silicon carbide kiln-furniture is in more general use in the United States than here.<sup>78</sup> Some practical considerations in the use of silicon carbide furniture concerning the improvement of the service life is given in the literature.<sup>79</sup> There is a feeling in this country that silicon carbide made into kiln-furniture may create a slight reducing atmosphere at the temperature of firing, which in most cases would be serious. It has been used as an addition to saggars with some success.<sup>80</sup> The performance of saggars for the electrical porcelain industry is excellently reviewed by R. G. Harris (*loc. cit.*), who deals with the standard mix and the influence of sillimanite, fused silica and silicon carbide. A patent has appeared<sup>81</sup> for the manufacture of silicon carbide refractories, such as setter tiles, by mixing finely divided carbon and silicon, shaping at high pressure and firing at  $1200^{\circ}$  to  $1500^{\circ}\text{C}$ . in a reducing or neutral atmosphere to complete the formation of silicon carbide. It is claimed that the crystals differ from the hexagonal silicon carbide crystals made by the usual electric-furnace method in that they are cubic and so finely crystalline that X-ray diffraction methods are necessary to demonstrate their crystallinity. Whether the properties of this material are different from the ordinary silicon carbide is not stated.

Carbon has many desirable refractory properties of which resistance to the action of molten metal and slag, and a strength not changed at high temperatures, are most outstanding. The first extensive applications of carbon in blast-furnaces originated in Germany, where carbon linings were used in the hearth.<sup>82</sup> These are accepted as being one of the best types of bricks for use in the hearth of a blast-furnace. The stability of carbon bricks in carbon monoxide under test conditions appears to be satisfactory,<sup>83</sup> and the trial of carbon-bricks in blast-furnace stacks to reduce scaffolding is recommended.<sup>84</sup>

Now that experience is accumulating on the use of all basic furnaces

for steel manufacture, it is possible that a more accurate assessment of their value can be ascertained. Reports on such furnaces are now appearing.<sup>85</sup> Figures showing increased production from 14.1<sup>86</sup>–40%<sup>87</sup> are published. Although much research work has been done previous to the use of basic materials in the steel-furnace, it can be expected that attention will continue to be devoted to basic refractories such as stabilised dolomite<sup>88</sup> and chrome magnesite<sup>89</sup> materials. The  $\text{CaO-MgO-Cr}_2\text{O}_3$  ternary system is being studied,<sup>90</sup> and some work on the  $\text{CaO-Cr}_2\text{O}_3$  system is published. This is an important section of the fundamental work necessary to obtain an adequate understanding of certain basic materials and throws some light on the poor results which have been obtained with chrome dolomite bricks in works practice.

An interesting observation is made by C. B. Clark and C. L. Thompson.<sup>91</sup> Repeated alternate oxidising and reducing conditions at 1200° and 1300° c. as well as repeated changes in temperatures above and below 1380° c. in an atmosphere of air, cause a spongy growth in iron oxide. This growth is apparently the result of repeated conversions of one oxide to another and it is suggested that the iron oxide deposited on refractories may have a destructive effect due to the spongy growth. It is doubtful whether the conditions to allow the iron oxide to convert, would prevail in practice, because iron oxide, in the reduced condition would react with the  $\text{SiO}_2$  in the brick, forming ferrous silicate which is fluid at the working temperature of most furnaces.

References have been made in these reports over a number of years to the unsatisfactory correlation of laboratory tests for slagging and service life. It is very difficult to simulate working conditions. The effect of slag-movement and slight changes in viscosity with changes in temperature make it most difficult to devise a quantitative test to indicate slag-resistance. Some of the tests depend on noting the depth of penetration, when the slag is melted on the surface of the brick; other tests try to take into account the brick-slag viscosity relationship. A further test on similar lines to these already existing ones is given in the literature.<sup>91</sup>

### Analytical and physical measurements

The use of the differential thermal analysis technique for identifying clay minerals has received much attention in the last few years. It affords a simple and inexpensive method of following the exothermic and endothermic reactions which take place when a clay mineral is heated through the range from room temperature to 1000° c.<sup>93</sup> The usual apparatus consists of two thermo-couples, one embedded in the sample and the other in the reference material. A modified differential thermal analysis apparatus<sup>94</sup> is described. It consists of two small thimbles which themselves form the differential couple by being joined in series at the top and having the leads to the indicator taken from the bottom of each thimble. The mineralogical changes in quartz, kaolin, and their mixtures when fired to 1350° c. have been followed.<sup>95</sup> The thermal analysis curves show two peaks over the cristobalite range. It is suggested that this is due to the clay on decomposing producing cristobalite of lower inversion temperature than that produced from quartz. On the other hand, the sensitivity of the differential thermal analysis method is

questioned. Small quantities of clay material with a weak thermal response, mixed with relatively large quantities of other clays cannot be detected: For instance, a clay which contained montmorillonite, shown by dye staining and petrographic examination, was not revealed by the thermal analysis.<sup>96</sup> Some further experience on this question has been described by R. E. Grim.<sup>97</sup>

Colorimetric and titration methods for the rapid analysis of cements are published.<sup>98</sup> H. Moritz<sup>99</sup> concludes, after comparing the spectrographic, polarographic, colorimetric, adsorptiometric and potentiometric methods, that taking all things into consideration, spectrographic analysis is the simplest, most rapid, economical, and versatile technique. This method has been used with success over a period of a year for the analysis of milled minerals and powered industrial chemicals.<sup>100</sup>

Further interest is indicated in the literature on grain-size analysis. A review of the methods for measuring particle size is given by H. Heywood.<sup>101</sup> The methods can be summarised as (i) sedimentation,<sup>102</sup> (ii) light scattering,<sup>103</sup> (iii) permeability,<sup>104</sup> and (iv) hydrometer.<sup>105</sup> There are no new developments. The existing methods are discussed and some modifications are suggested. It is stated that the permeability method can only be used for comparative determinations. The values of gas permeabilities vary with the nature and pressure of the gas used, but the method has already shown its value in many industrial applications.

A useful summary of the applications of X-rays to ceramic problems is given by G. L. Clark.<sup>106</sup>

## Firing

With the economies demanded in fuel consumption, the heavy clay industries have for some years been experimenting with automatic stoking. A certain amount of success has been achieved in reduction of fuel consumption. Figures in the order of 11% are reported,<sup>107</sup> and some anticipate a saving of 20%.<sup>108</sup> At present, the saving in fuel is offset in some instances by the production of more rejects. R. J. Parker (*loc. cit.*) found that the products from a salt glaze pipe-kiln after firing by means of a stoker were not equal to the hand-fired products. The two main troubles which appear to be experienced with automatic stoking are a steep temperature gradient in the oven, due to failure to obtain adequate length of flame and also a big risk of fly ash which tends to spoil many articles. Some success with automatic stoking has been achieved according to T. R. Lynan.<sup>109</sup> The results of five firings of silica shapes in a round down draught-oven indicated that the temperature required for silica bricks can be reached in a shorter time than with hand firing. Probably with different designs of flue-systems and in collaboration with stoker manufacturers it will be possible to overcome many of the problems in order to make a success of firing by automatic stokers.

The well known fact that it is necessary to fire thick ware very slowly through the critical range when contraction is rapid is discussed by Y. Letort.<sup>110</sup> He has calculated that using a specimen 8 in. thick and which contracts 0.5% during firing, the differential stress between the outside and inside may amount to 140 lb./sq. in.

Silicon carbide resistors for furnace-heating have been used for many years. The construction of a small electric-kiln using these elements is given by M. S. Nelson.<sup>111</sup> The biggest objection to this type of resistance is the change in resistance with use, which necessitates auxiliary equipment such as automatic regulators.

Some comparison of fuel consumption of the coal-fired frit-kiln as used in the pottery industry and a commercial glass bottle furnace is published by R. J. Waller and M. Francis.<sup>112</sup> The amount of fuel consumed per unit weight of frit is 1.2 to 1 compared with that of a glass bottle furnace which is 0.5 to 1.

The two-decker and three-decker round-kilns are not used in this country but are in use in Germany. The top decks are heated on the up-draught principle by the gases coming directly from the lower decks through flues in the floor and then upwards to the stack. The consequent short time of contact with the setting in the top deck of a three-decker oven, prevents the attainment of a sufficiently high temperature by the time the other decks have reached their peak temperature. A simple improvement is suggested<sup>113</sup> which applies the down-draught principle to the top deck and enables all three decks to reach the final temperature simultaneously. The advantage of replacing muffle kilns of the intermittent type by a tunnel for decorating purposes, with a consequent saving of fuel, is also recorded by the same author. In this country the intermittent-kiln for decorating is almost obsolete. A review of the design of tunnel kilns for firing any type of clay ware is published by R. G. Le Grip.<sup>114</sup> Some of the newer types of tunnel ovens using gas are using the radiant tube principle.<sup>115</sup>

## Cements

There appear to be two factors which affect the properties and crystallisation of aluminous cement according to J. Brochard.<sup>116</sup> When he compared the rate of crystallisation of pure mono-calcium aluminate with aluminous cement he found an appreciable difference. At a particular temperature of 30° c., crystallisation in the case of aluminous cement does not commence until after about 2 days, whereas pure mono-calcium aluminate crystallises after about 6 hours. This difference is ascribed to the existence of critical limits of  $p_H$ , between which crystallisation of hydrated aluminates is retarded. The ratio of the  $\text{CaO} : \text{Al}_2\text{O}_3$  in solution in the case of the aluminous cement gives a  $p_H$  between these limits at 30° c. and the rate of crystallisation is reduced. Also at 30° c. the crystals of the hydrate from the pure aluminates are rapidly transformed from the hexagonal to the cubic form, but the change does not occur in the case of the cement until 50° c. The results are considered to explain the more rapid setting of aluminous cement at temperatures above 30° c. The loss of mechanical strength which is observed when aluminous cements are heated is ascribed to change in crystalline form from hexagonal to cubic.

Much reliance is placed in many quarters on the chemical composition of the mix for the manufacture of Portland cement. It is believed by some<sup>117</sup> that efficient and economical clinkering is controlled by the chemical composition of the mix and the intensity of burning. On the

contrary D. Dutron<sup>118</sup> and A. Rebuffat,<sup>119</sup> while agreeing that the chemical composition and the burning are important, state that these give little indication of the physical and mechanical properties of the Portland cement. The cooling of the clinker is important. The clinker, which consists essentially of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ , if cooled quickly, may contain considerable proportions of  $2\text{CaO}$ ,  $\text{SiO}_2$ , and  $3\text{CaO}.\text{SiO}_2$ , accompanied either by varying amounts of glass and crystalline  $3\text{CaO}.\text{Al}_2\text{O}_3$  or accompanied by  $3\text{CaO}.\text{Al}_2\text{O}_3$  and  $5\text{CaO}.\text{Al}_2\text{O}_3$  in the case of slow independent crystallisation from the liquid phase. Cooled slowly the same clinker consists of  $3\text{CaO}.\text{SiO}_2$ ,  $2\text{CaO}.\text{SiO}_2$ , and  $2\text{CaO}.\text{Al}_2\text{O}_3$ . The rate of cooling therefore alters the mineralogical composition, which is of some importance.

A review of the chemical research on Portland cements is given by R. H. Bogue.<sup>120</sup> The possible compounds and solid solutions which exist in the cement are given. According to this author the hexagonal form of  $3\text{CaO}.\text{Al}_2\text{O}_3$  aq. does not exist, and the substance previously designated as such is a mixture of  $2\text{CaO}.\text{Al}_2\text{O}_3$  sq. and  $4\text{CaO}.\text{Al}_2\text{O}_3$  aq. The setting process is considered and evidence is given in favour of the film theory, but H. Kuhl<sup>121</sup> believes that set cement is a shrunken gel, probably hydrated tri-calcium di-silicate. R. H. Bogue (*loc. cit.*) confirms that each cement has a gypsum requirement for optimum retardation.

L. Chessevent<sup>122</sup> confirms a well-established fact that the swelling of plaster depends on the ratio of plaster to water and that it is diminished in the presence of  $\text{K}_2\text{SO}_4$  and many other salts.

The use of entraining agents for the purpose of increasing durability of concrete and their effect on durability, consistency and strength are discussed by H. L. Kennedy.<sup>123</sup> The author discusses the effect of richness of mix, sand content, and grading, consistency and temperature of the mix on the air content. He points out that the air content of cement can vary, when a constant percentage of air entraining agent is added, if any variation occurs elsewhere.

An interesting observation on the damage in concrete tanks used for cooling brine is made by C. Wastfund.<sup>124</sup> He concluded after estimating the salt and "free water" content at different distances from the inner surface that damage was due to stresses set up in the layer where the freezing temperature of the liquid phase of the concrete lay within the range of fluctuation of the brine temperature. A suggestion for overcoming the trouble is to add to the concrete-mix a substance such as sulphonated fatty alcohol which will lower the freezing point of the liquid-phase without itself damaging the concrete.

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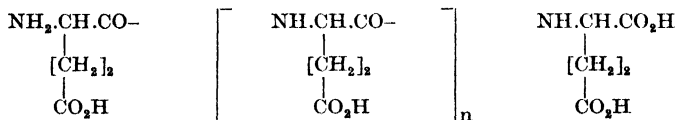
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# THE PROTEIN FIBRES

By DAVID TRAILL, Ph.D., F.R.I.C., F.T.I.

ATTENTION was drawn last year to a new line of attack on protein structure arising from the development of the neglected Leuchs polymerisation and the synthesis of polypeptides. Using this synthesis, Hanley, Waley, and Watson<sup>12</sup> have now prepared polyglutamic acid, with an estimated molecular weight of 15,000.



Astbury, Dalglish, Darmon, and Sutherland<sup>10</sup> describe work of which the general object is to synthesise as many as possible, first of homogeneous polypeptides from single amino acids and secondly co-polymers of two or more amino acids and then by X-ray, infra-red, and accessory techniques to study their properties in relation to those of proteins of analogous composition. Films of such synthetic polypeptides have been made and studied but no fibres have yet been described.

Di- and tri-glycine, like glycine, do not absorb water but higher peptides, tetra- and hexa-glycine show an increasing absorption.<sup>21</sup> Polyglycines of 44 and 59 units give, on a weight basis, almost identical vapour-phase moisture absorption isotherms showing clearly that the peptide groups are primarily responsible for the absorption of water by these polypeptides. The peptide chain in the glycine polymers absorbs almost the same amount of water as does the peptide backbone in silk. Assuming that the peptide chain in any protein absorbs the same amount of water as the polyglycine chain, the peptide chain accounts for 46% of the water absorbed by casein and 70% of that absorbed by zein at 60% relative humidity. Absorption data on polyglycines and proteins when plotted as the logarithm of the absorption against relative humidity are linear over 30–80% relative humidity.

In a consideration of the principles of structure of synthetic fibres, Mark<sup>25</sup> has pointed out that samples of different mechanical properties can be made from the same polymer, depending on the state of order of the molecules, the properties being influenced by the chemical nature and structural details of the molecules and by the arrangement of the molecules in the sample. Natural and synthetic polymers (tabulated) have a molecular weight of 20,000–1,000,000 and degree of polymerisation (DP) of 100–5000. A minimum DP of 40–80 is necessary for mechanical strength; thereafter, tensile strength increases with DP up to about 250 and is little influenced at DP above 600. Little is known about the effect of molecular weight distribution, but the presence of 10–15% by weight of low DP constituent is detrimental to strength, etc. In polymers, the chains show a tendency to curl up rather than to remain extended.

They are attracted intermolecularly by van der Waals forces, and mobility is hindered. The intrinsic flexibility of the chains is important. The arrangement of the molecules in crystals and polymers is discussed with reference to frozen isoprene and frozen rubber. Heating the latter decreases the intermolecular forces and destroys geometrical order, giving entangled molecules and thus accounting for rubbery properties. Glasses are liquids of high viscosity and rubbers are liquids of long-range molecular entanglement, having rapid internal and slow external Brownian movement. Loss of shape under stress can be prevented in polymers by insertion of chemical cross-linkings, polar groups capable of giving strong intermolecular attraction, or fillers.

## Wool

### *Electron Microscopy*

A study of organic fibres by electron microscopy has been undertaken by the National Bureau of Standards.<sup>26</sup> A simplified shadow replica technique has been developed by Swerdlow and Seeman whereby fine details of the morphology of wool, both in its natural state and after various treatments have been revealed. It consists essentially of pouring a suitable solution of either ethyl cellulose or polystyrene on to a glass slide, laying the fibres on the thin thermoplastic film produced, covering with another glass slide, and heating the damped ensemble for 20 minutes at 90° c. The replica thus produced is thinly coated with evaporated chromium for added contrast and three-dimensional aspect. The replica, supported on a specimen screen, can then be examined in the electron microscope. Present theories of the structure of wool have been confirmed by this method. The study has been extended to cover the field of wear and tear of garments. The method of mechanical abrasion due to Schiefer was used. The photomicrographs are striking; the magnification achieved is about 9000 times.

Wool keratin is considered to be completely soluble in sodium sulphide. Lindberg, Philip, and Gralén<sup>52</sup> find that there is an insoluble fraction, not more than 0.1%, which causes opalescence in the solution and can be separated by centrifuging. This fraction consists mainly of thin membranes which were studied under the electron microscope and were found to be 50–100 Å. in thickness. The authors assume that they have a different composition from ordinary wool keratin. Their experiments indicate that these membranes are located in the surface layer of the wool and may have an important bearing on surface phenomena.

### *The disulphide bond*

The cross-links between the polypeptide chains of keratin are the salt links, which result from the diamine and the dicarboxylic acids present in the molecule, and the disulphide bond of cystine. The salt links are hydrolysed with water and so the wet strength of wool is principally due to the disulphide bonds. Harris and Brown<sup>1</sup> have drawn attention to the importance of these cystine cross-links. They are of major importance in controlling the strength and elastic properties of the fibre. They are also used to explain the mechanism of permanent set, although the evidence is indirect. The disulphide bond of cystine is susceptible

to attack by various chemical reagents, moths and enzymes. For some purposes, therefore, replacement by more stable linkages, or the introduction of new linkages, is desirable. The earlier work on re-forming cross-links from the hydrolysed disulphide bonds by reaction of the -SH groups with propylene dibromide has been reviewed.

Wool modified by reducing with thioglycollic acid and relinking with alkylene dihalide has never gained industrial importance because of the excessive cost. A search for more practical methods was therefore undertaken. Inorganic reducing agents like hydrosulphites and sulphoxylate-formaldehyde are both inexpensive and are known to have a strong reducing action on the disulphide bond. In treatment with these agents at elevated temperatures wool was considerably damaged and subsequent treatment with alkylene dihalides did not restore the desirable mechanical properties. Apparently rupture of the disulphide bond at high temperatures facilitates molecular rearrangement. Attempts were therefore made to rebuild new stable linkages as rapidly as disulphide cross-links are ruptured, since it was thought that modified wool with desirable properties could thus be produced.

Harris and Brown<sup>48</sup> describe a new one-step process for hydrolysis of the unstable cystine bond and formation of a more stable cross-link, the wool being reduced with sodium hydrosulphite or sodium formaldehyde sulphonylate and then linked immediately by action of an alkylene dihalide or formaldehyde to give a stable  $-S.(CH_2)_n.S-$  link. The alkali-sensitive cystine group is thus replaced by one far less reactive, the bis-thio ether linkage. The process, which gives a wool of excellent handle, is cheap and more rapid than the earlier two-stage process. It may be used to stabilise wool against damage during treatment with oxidising, reducing, and alkaline reagents.

Krist<sup>8</sup> has presented another method of stabilising wool by cross-linking the polypeptide chains with resistant bridges, using agents such as chloromethyl ether, without attacking the disulphide bond.

The fibres are preheated with a solution of the bis-chloromethyl ether of 1 : 6-hexandiol in carbon tetrachloride, using pyridine or sodium carbonate as buffer. A series of chloromethyl ethers of mono- and polyvalent alcohols were tested. In each case the ether was dissolved in carbon tetrachloride and buffered with pyridine and in each case the solubility of the wool in alkali was substantially lowered. For technical application the wool may be treated in batches in a dry-cleaning apparatus.

If the disulphide bond is reduced before reaction with the dihalide, a thiazolidine ring is formed with the -SH group. Although no cross-linkage is formed the product is alkali-resistant. Considerable shrinkage of the fibre takes place on boiling in sodium carbonate solution. This does not occur when a cross-linkage is formed as in the case of pyridine.

Elöd<sup>9</sup> worked with wool pre-treated by Krist's method with butandiol-bis-chloromethyl ether. He compared the mechanical and elastic properties of the fibre with untreated wool fibres in a Deforopt apparatus. The length of the fibre was measurable to 0.05%. The steps in stretching proceeded by 0.5% increased to 3% and thereafter by 1 and 2%. After each stretching the elongation and load were determined. The dry

tensile-strength and the dry elongation decreased as a result of treatment. The modulus of elasticity increased.

The solubility of the treated wool in sodium hydroxide decreased considerably. The treated wool contained 8%  $-\text{CH}_2-\text{O}-(\text{CH}_2)_4-\text{O}-\text{CH}_2-$  groups and the cystine content was lowered in proportion. In the case of both treated and untreated wool the cystine content is reduced by boiling in sodium carbonate solution. The treated wool stands up to treatment with sodium carbonate and the untreated wool disintegrates completely. Consequently, the improved resistance of the treated wool is not due to protection of the cystine group and a decreased cystine content is not always an indication of wool damage.

Treatment with butandiol-bis-chloromethyl ether decreased the super-contraction of the fibre in sodium hydroxide indicating a higher alkali resistance. Resistance to reducing agents is also increased. The conclusion drawn is that improved alkali resistance of alkylated wool is not based on a reinforcement of the cystine linkages but on new sulphur-free cross-linkages between the peptide chains.

An American method of moth-proofing woollens, known as "Boconising" employs a compound which is said to combine with wool at the disulphide linkages.<sup>27</sup>

### *General*

Stokes<sup>14</sup> has described research carried out primarily on wool or human hair which has provided evidence on the molecular structure of keratin. In these types of fibres, cortical cells constitute the bulk, and the physico-chemical properties are readily explained in terms of the cystine and salt cross-links between the folded peptide chains. Histochemical examination of various fibres from the coats of carnivores and rodents show wide variations in micro-structure, chemical constitution, and reactivity, the variations being responsible for differences in the fibres longitudinally and laterally. Results of histochemical tests have been correlated with stress-strain diagrams and axial contractions of non-medullated fibres. The reaction of cuticle, cortex and medulla cells with specified reagents suggests that both structural and chemical factors may be involved in determining the properties of various types of keratin. Variations in the end-products of biochemical and physical changes occurring in the cells of the hair follicle are expected to give information on the mechanism of keratinisation processes. The results are of importance in fur dyeing and in the manufacture of hatting felts and brush bristles.

In a literature review, Elöd and Zahn<sup>2</sup> conclude that the action of alkali on wool keratin is not sufficiently specific to shed much light on the properties of the fibre. The wool proteins are split by micellar surface action and X-ray diagrams of keratin show little difference before and after the action of the alkali. At room temperature the action of water on keratin produces a reversible inter- and intra-micellar action, involving the polar groups; at 60–80° C., hydrolysis of the cystine predominates, whilst at temperatures above 100° C. irreversible splitting of the micelles occurs, involving denaturation and supercontraction of the fibres. Most of the cystine present is not a constitutive part of the micelle but acts as a binder between the micelles. The relationships between the chemical

and physical and structural properties of keratin (strength, elasticity, super-contraction, permanent set, and fine structure of the micelles) are discussed.

Working on partial acid hydrolysates of wool, Consden and Gordon<sup>28</sup> removed the acidic amino acids and peptides from a partial hydrolysate of wool by chromatography on Amberlite IR-4 resin. The solution was oxidised to convert cystine compounds into cysteic acid compounds. The latter were then separated by re-chromatographing on Amberlite IR-4. The mixture of cysteic acid and peptides of cysteic acid thus obtained was next subjected to ionophoresis. The various bands, moving towards the anode, were then worked up for analysis on paper chromatograms. The following dipeptides were identified: cysteicyglycine, cysteicylalanine, glycylcysteic acid, serylcysteic acid, alanylcysteic acid, threonylcysteic acid, cysteicylvaline, cysteicylleucine, leucylcysteic acid, and phenyl-alanylcysteic acid. A number of higher peptides were present; the proportion of proline residues in these appeared to be high.

The permanent set which strained wool fibres acquire in steam or boiling water is believed to be due to two consecutive intramolecular reactions, namely, hydrolysis of the disulphide bonds to give sulphenic acid and mercapto side-chains, followed by condensation of the sulphenic acid, or the aldehyde to which it gives rise on decomposition, with the basic side-chains of lysine and arginine. Disulphide bond breakdown promotes relaxation, and the relaxed structure is stabilised by the new cross-linkages. The main evidence that the basic side-chains play an essential part in the linkage-rebuilding reaction is the failure of deaminated fibres to acquire a permanent set in steam. It seemed desirable that further evidence should be obtained because of recent suggestions that the breakdown and re-formation of hydrogen bonds between the peptide chains may be sufficient to impart a permanent set to strained fibres. The setting power of wool treated with 2:4-dinitrofluorobenzene has therefore been examined.

Experiments with purified Lincoln root wool show that the setting power is considerably reduced by treatment with 2:4-dinitrofluorobenzene. The authors, Speakman and Farnworth,<sup>53</sup> therefore, think it is reasonable to conclude that the free amino groups of wool play an essential part in the cross-linking reaction which is responsible for permanent set. A comprehensive review of the mechanism of set and super-contraction has been made by Blackburn and Lindley.<sup>50</sup>

An attack has been made on the damaged wool problem from the physical side by Engeler.<sup>13</sup> Measurements have been made on the Schopper fibre dynamometer using normal wool and wool after different degrees of exposure to sunlight. The results show that for the practical behaviour of the fibre the breaking energy is a more important factor than either strength or extensibility considered separately. Measurements of strength and extension are suitable for indicating changes in properties of the fibre and serve to confirm the results of chemical tests.

Under suitable conditions methyl methacrylate and acrylonitrile are polymerised within wool fibres which have been immersed in aqueous suspensions of the corresponding monomers.<sup>3</sup> Wool fabrics are modified and rendered unshrinkable by this process.

Melamine resins have been shown to be uniformly distributed within the fibre structure, and there is no obvious change in wool fibre scale-structure after melamine resin treatment. Marshall and Aulabaugh<sup>4</sup> describe a dye-staining and sectioning technique for quantitatively detecting the resin which makes possible a direct, visual determination of the location of melamine in treated wool fibres.

### *Scouring*

Dubeau and Vincent<sup>5</sup> describe scouring processes and state that the highest ratio of scouring results from maintenance of the  $\text{Na}_2\text{CO}_3$ :  $\text{NaHCO}_3$  ratio of the scouring liquor between the limits 1 : 0.5 and 1 : 2. The advantage of using non-ionic detergents (reaction products of ethylene oxide and alkyl phenols) for the final stages of the scour are indicated by Borghetty.<sup>6</sup>

The problem of scouring-out mineral oils used for wool lubrication has been complicated by presence of excessive residues from wool scouring due to shortages of soap and alkali.<sup>7</sup> Sodium chloride is used in conjunction with soda, soap and sulphated fatty alcohol. The use of ammonia, both in the scour and as an assistant in washing-off accentuates uneven scouring. Uneven dyeing is more related to uneven residual grease than to the total amount. A preliminary scour in 0.6%  $\text{Na}_2\text{CO}_3$ , 0.6%  $\text{NaCl}$ , and 0.5 lb. of sulphated fatty alcohol per piece at  $p_H$  9.5 for 10 minutes, and washing-off for 5 minutes, followed by the main scour for 30 minutes and washing-off, gives satisfactory results. Further improvement must be effected by a change in dyeing methods.

Recently there has been very considerable interest in synthetic detergents for scouring wool, mainly because of the high price and scarcity of soap, and it has been found that, using detergents, a saving in soda ash, which is still in restricted supply, can be effected. Morris<sup>30</sup> has considered the use of synthetic detergents. Extended practical trials have shown that non-ionic detergents are particularly attractive for raw wool scouring.

The composition of the wax of merino wool alters during storage due to oxidation. The content of neutral oils and alcohols decreases, whilst the fatty acid and ester contents increase. Commercial lanoline exposed to the atmosphere behaves similarly. Freshly isolated non-saponifiable matter from wool wax, kept for 3 months (including 500 hours at 60°), yields a mixture of unoxidised  $\text{C}_{27}$ -alcohols, neutral  $\text{C}_{54}$ -esters of monobasic  $\text{C}_{27}$ -acids, neutral  $\text{C}_{81}$ -esters of monobasic  $\text{C}_{54}$ -acids and half  $\text{C}_{81}$ -esters of dibasic  $\text{C}_{54}$ -acids, and also  $\text{C}_{27}$ -fatty acids. Gilliam<sup>20</sup> suggested that the  $\text{C}_{27}$ -alcohols are oxidised to  $\text{C}_{27}$ -hydroxy acids, the esters of which interact either with an alcohol or a dihydroxy acid to give the above products or other possible polymers or cyclic esters.

### *Dyeing*

Wool fibres and fabrics can be dyed without damage using vat colours and conventional dyehouse equipment.<sup>31</sup> A high sodium hydroxide concentration is used, but no protective agent. For fabrics, two methods are available. In the first, the vat colour is reduced prior to dyeing. The wool is wetted out on a reel machine or piece dye kettle with a wetting agent; to this bath, comprising nine-tenths of the total dyeing

volume, 0.25–0.5 ounces per gallon of sodium hydroxide and 0.7–1.0 ounces per gallon of sodium hydrosulphite are added; after running 5–10 minutes, the reduced colour is added slowly; dyeing is done by running 30–60 minutes at 90° F., 10 minutes at 100° F., and 10 minutes at 110° F. 2–6 ounces per gallon of common salt are then added, and running continued for 10–20 minutes. At 110° F., additions should be made if necessary to the sodium hydroxide and hydrosulphite concentrations. The sodium hydroxide remaining in the bath is neutralised to sodium carbonate by the addition of sodium bicarbonate. The material is finally rinsed, oxidised with sodium perborate, and soaped. In the second method, pigment colour is added to the dye kettle, with no reduction prior to dyeing; the same dyeing cycle is followed as for the reduced method. For loose wool and worsted tops, circulating machines are used; the procedure is almost the same as for piece goods, except that the sodium bicarbonate is added to a fresh bath. The pigment method is unsuitable for loose wool and tops, but is more suitable than the reduced method for dyeing wool-viscose mixtures. Vat dyes of the "Ponsol" range are recommended. Illustrations show comparisons of tinctorial strengths of vat dyes on wool and cotton, and fastness on wool of vat and acid colours and of vat and chrome colours.

Any difference in fastness to light between dyeings on wool and chlorinated wool appears to be of no practical significance.<sup>29</sup> In the production of tone-in-tone effects dyeing under neutral conditions with metalliferous dyes, the fastness to light of both the light (unchlorinated) and dark (chlorinated) dyeings is of the same order as that of similar dyeings made under the normal conditions using 6 to 8% sulphuric acid.

With the level-dyeing acid dyes, which possess only moderate to poor fastness on wool, the reduction in fastness properties of the chlorinated wool is appreciable. With milling-type dyes this reduction is less important and in some cases negligible. With chrome, metalliferous and direct cotton dyes, chlorinated wool has good fastness properties.

Tucker<sup>32</sup> has compared the dyeing of fur felt hats with wool dyeing. He describes types of machines and methods commercially used for dyeing raw stock and fur felt hat bodies and gives evidence in support of the theory that certain dyes specifically promote fibre damage. An experimental machine is described which produces penetration of felt at a felt-liquor ratio comparable with that used in the factory operation.  $p_H$  Extraction rate curves are given for samples of fur felt and of wool yarn dyed in this machine. Although the exhaustion of dyes on wool is generally greater than on fur felt, at the same  $p_H$ , the difference in the  $p_H$  range 2–4 is generally less than 5%, which does not explain the fact that it takes almost twice as much dye to obtain the same shade on fur as on wool. Flexing tests were made on a commercial machine and tensile-strength tests on a standard Scott tester. A special method was adopted for sampling. The results are given of the effects of methods of dyeing upon flexing and tensile strength.

### *Spinning*

Specifications for oleic acid and olive, arachis and mineral oils for use as lubricants for yarn spinning, and methods for their removal are

discussed.<sup>15</sup> Applications of mineral oils and greases, and their emulsions, are reviewed by Bulwer,<sup>16</sup> who also discusses their removal from the treated materials.

The spinning of worsted yarn on the American system is described by McConnell,<sup>17</sup> who considers the machinery, its operation, fibre lengths which can be processed (not less than 1.5 in.) and the type and counts of yarn produced by a process of three stages of drawing, roving and long draft spinning. A report on American and Canadian developments is given by Pitcher.<sup>18</sup> A colloidal dispersion of silica (trade name Syton) has been used in worsted spinning to give yarns and fabrics of greater strength.<sup>19</sup>

## Silk

Chromatographic work by Polson, Mosley, and Wyckoff<sup>22</sup> on silk hydrolysate shows that the serine content is high but that there is little or no phenylalanine. The tyrosine content is less than and the alanine content greater than shown by other methods. The presence of valine is stated to be shown for the first time but it must be remembered that in 1944 McMahon and Snell found valine and arginine in silk fibroin using a microbiological method. The present chromatographic work does not support the presence of methionine.

Sericin can be extracted from disintegrated silk cocoons, free from pupae, by boiling in water for not more than 8 hours.<sup>23</sup> The extract is evaporated and dried finally at a temperature not above 50° *in vacuo* to give a powder. A spray dryer, similar to that used for drying milk and having a special pressure-operated spraying nozzle orifice, is described. Extinction coefficient ( $E/\lambda$ )-curves of sericin solutions show a characteristic waveband at 2730 Å. corresponding with that due to presence of tyrosine. Curves relating  $p_H$  and  $E$  for various concentrations of sericin are given; the buffering capacity is linearly proportional to the concentration of sericin. Optical, electrical, swelling, and viscosity methods give an isoelectric point for sericin of 4.1. Sericin obtained on the large scale from silk-industry waste water as a dry powder may be used for sizing and as a substitute for agar in bacteriological media.

## Nylon

Glatt and Ellis<sup>24</sup> report a study of the absorption spectra of nylon with polarised infra-red radiation. The  $-\text{CH}_2-$  absorption is quite similar to that of polythene. Nylon crystalloids consist of parallel sheets, the backbone planes lying in the sheets with adjacent chains held together by intermolecular N-H...O bonds which extend perpendicularly to the chain axes. The second harmonic of the perturbed N-H stretching vibration is almost certainly responsible for a band which appears at 6523  $\text{cm}^{-1}$ , as well as for at least some of the neighbouring structure. A strong 4883- $\text{cm}^{-1}$  band, with weak neighbours, is attributed to N-H bond, stretching and deformation vibration. The third harmonic of the perturbed C : O vibration is probably responsible for a band at 4975  $\text{cm}^{-1}$ . Spectrograms of molten nylon kept at 300° C. gave evidence of rupture of the intermolecular N-H...O bonds. Specimens kept at 200° C.,

i.e., below the melting point ( $260^{\circ}\text{C}$ .), show the bands characteristic of both the bonded  $\text{N-H} \dots \text{O}$  (perturbed) and free  $\text{N-H}$  groups.

The density of nylon filaments has been determined by three methods, all of which involved immersion in organic solvents.<sup>35</sup> The densities of undrawn and drawn filaments are 1.1339 and 1.1384 respectively, at  $25^{\circ}\text{C}$ . Annealing either the drawn or undrawn forms at the highest temperature possible short of melting increases the density to 1.1465. The temperature coefficient of the density as measured at room temperature is greater for the drawn form of nylon than the undrawn after annealing has taken place. The density of perfectly crystalline nylon calculated by Bunn and Garner<sup>36</sup> from X-ray data is considerably higher (1.24) than the highest value obtained by the present authors on annealing.

Miklowitz<sup>24</sup> used a high-speed tensile-testing machine to measure the stress-strain characteristics of unoriented nylon under an applied uniaxial tensile stress. The yield point elongation in nylon increased almost three-fold for a 10,000-fold increase in the speed of stretching. The true yield stresses and yield load stresses increased almost twofold over the same range. The first sharp drop of load, or any succeeding drop of load after the visible beginning of the yielding process, came simultaneously with the formation of a double yield front. As the speed of deformation increased, the length of the advancing yield front decreased. As the rigidity of the testing machine increased, the load-drop became steeper from upper to lower yield-point. The upper yield-load stress increased with increase in machine rigidity. The yield-point elongation is composed of the strain in a section of material due to the plastic yield front passing over it, and the strain due to the continuous action of the load on this section as the plastic discontinuity advances to yield other sections of material. The effect of two advancing yield fronts is discussed. The relation of the data to similar data for mild steel is considered.

Milliard,<sup>37</sup> in an article on the properties of nylon and its processing preparatory to weaving, covers yarn processing from the nylon package, as delivered by the spinner, to the segregation of warp and weft yarns. He therefore describes re-winding, throwing, twist setting and doubling. The properties of the yarns are also described.

The specific strength of normal weaving yarns is 4.8 grams per denier, but 8 grams per denier has already been achieved on the pilot plant scale. The breaking elongation lies between 22 and 15%. The work of rupture is very high. Wetting causes a loss of 10–15% in strength which is recovered on drying. The moisture regain is approximately 4%. Un-sized nylon yarns elongate fairly readily at low loads, consequently processing tensions merit careful attention. Shrinkage on wetting of mixed yarns and fabrics can reach 4% in cold water and 8% in boiling water. In boiling water twist set yarns may shrink up to 2% and wet fabrics less than 1%. Nylon is inherently flameproof; it does not blaze when brought into contact with a flame, but melts and forms a round hard bead. The optimum ironing temperature for crease removal is  $180\text{--}200^{\circ}\text{C}$ . but temperatures above  $220^{\circ}\text{C}$ . should be avoided. The ideal method of setting employs saturated steam under pressure. Nylon is immune to attack by all micro-organisms. It has good resistance to chemical attack, being unaffected by most organic acids, carbon disulphide,

carbon tetrachloride, dilute alkalis, soaps, petrol, benzene, and alcohols. It is dissolved by formic acid, phenol, *m*-cresol, cresylic acid, and xyleneol. It is degraded by strong oxidising agents and by concentrated mineral acids.

A comparative study of the rates of photochemical degradation of viscose rayon, silk, nylon and cotton yarns undyed and dyed with different vat dyes has been made by Egerton.<sup>33</sup> The yarns were exposed to sunlight in atmospheres of different compositions and relative humidities, and the consequent losses in tensile strength were used as a measure of the extent of photochemical degradation. The rate of degradation is dependent upon the presence of oxygen in the surrounding atmosphere, and for all the textile materials examined the degradation is chiefly due to oxidation processes. On exposure in air, the effect of humidity on the rate of degradation differs widely with the different textiles. The rate is greater in humid air than in dry air with both silk and cotton, the difference being particularly large when these textiles are dyed with sensitising vat dyes of high activity. The rate of degradation of nylon yarns dyed or undyed is, however, but little affected when the relative humidity is changed from 0 to 100%.

The degradation of silk is sensitised as strongly by some indigoid dyes as by the most active anthraquinonoid dyes, and the action is not confined to the yellow and orange representatives. The degradation of nylon is also strongly sensitised both by some anthraquinonoid and by some indigoid vat types, not all in the yellow and orange shade range. Those dyes which are active on the cellulose fibres are all active on nylon, and, in addition, some, not very active on the cellulose fibres, activate the degradation of nylon. All dyes, active on nylon, as well as some that are not, are active on silk.

The relative activity of the same vat dye on the different textiles depends upon the humidity of the air. In moisture-saturated air the effect of active vat dyes is generally greatest on silk, followed in order by nylon, cotton, and viscose rayon. In dry air the greatest effect is shown by the vat dyes on nylon. Observations are recorded on the rate of photochemical degradation of undyed viscose rayon delustrated with titanium dioxide, and of dyed and undyed nylon similarly delustrated.

Wittner<sup>38</sup> reviews the various modern methods and dyes for dyeing nylon. He briefly explains the du Pont "pad steam" method, and an improved method suggested by the Ciba Co. He claims that the addition of gum tragacanth in conjunction with certain dyes improves the evenness of dyeing achieved by the du Pont method. Clapham,<sup>39</sup> in a similar discussion, outlines the procedure for hosiery and piece goods as well as the dyeing of yarn and raw stock. Dyeing of nylon staple and mixtures is described by Fidell.<sup>40</sup>

The quantity of nylon in a mixture with viscose, wool, and cotton can be determined by dissolving the nylon in 90% formic acid.<sup>41</sup>

### Regenerated protein fibres

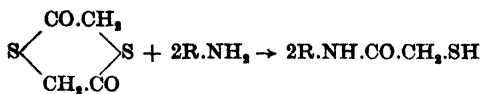
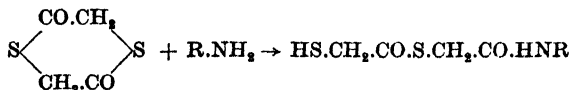
Recent developments in the chemistry of the artificial protein fibres are again reviewed, this time by Hoover, Kokes, and Peterson,<sup>42</sup> who

emphasise the difference in amino acid content of the various proteins. New experimental results of thermo-elastic analysis of protein fibres and determinations of peptide chain length in proteins (*beta*-lactoglobulin, bovine serum albumin, casein, zein, and soyabean protein) by end-group analysis are presented. These indicate that the major industrial proteins have a somewhat low chain length.

At various times attempts have been made to extrude dispersed keratin into fibres. In general the attempts have not been very successful, and this lack of success has been ascribed to the lowering of the molecular size caused by the process of dissolution or by the hydrolysis of the polypeptide chains of the protein by the aqueous alkali. Wormell<sup>42</sup> thinks this unlikely and believes that the failure was probably due to the adoption of unsuitable extrusion techniques. After dissolving wool in aqueous sodium sulphide, the degradation product from wool may be isolated by simple precipitation with the appropriate quantity of hydrochloric acid, the precipitate washed, dried, ground to a fine powder. This powder may be blended with casein and re-dissolved in dilute alkali to form a solution from which fibres may be easily extruded. The filaments, after hardening, stretching, and re-hardening show orientation when subjected to X-ray examination.

In neutral or slightly acid solution, formaldehyde introduces methylene bridges between amines on the one hand and the reactive hydroxyl groups of phenolic and imidazole rings on the other.<sup>44,49</sup> The phenols react to completion within a few days at room temperature. The linkage is resistant to acid hydrolysis. Experiments with gramicidin suggest that condensations joining indoles, amines, and formaldehyde under similar conditions may occur with the  $-NH-$  group of the indole ring. These reactions take place with similar ease also in proteins containing the necessary groups. They supply a means of introducing a great variety of reactive cyclic compounds into proteins, and of amino compounds into gramicidin. The problem of the mechanism of the reaction of formaldehyde with proteins, however, has not yet been elucidated.

Schoberl<sup>51</sup> has introduced sulphur synthetically into proteins by treating, for example, casein with thioglycollic acid in weak alkaline solution,  $p_H$  7-11. He found that he must use aged thioglycollic acid and not freshly distilled acid. In aged thioglycollic acid and in distillation residues there are thioglycollides present and these have been found to be active substances. In aqueous solution thioglycollides can combine with amines, such as aniline, forming thioglycollic acid amides and this explains the mechanism of the sulphurising action



It has been concluded that, in proteins, the free amino groups of the lysine residues react with thioglycollides forming sulphydryl proteins.



This is confirmed by Schoberl's results which show that the increase in sulphur corresponds to a decrease of free amino groups.

The introduction of the sulphydryl groups is achieved in the absence of atmospheric oxygen. The caseins treated in this way react with formaldehyde with a reduction of  $-\text{SH}$  groups but no loss in sulphur. The  $-\text{SH}$  groups can be oxidised to disulphide groups but this requires further study.

### General

A considerable amount of work is being carried out in various parts of the world on the physical properties of fibres especially on plasticity and resilience. Meredith and Peirce<sup>45</sup> describe a cyclic loading test in which small extensions are repeatedly applied to a yarn or cord and the total irrecoverable extension, that is, the cumulative extension, is measured. It is designed particularly to discriminate between a plastic extension leading to rupture and an elastic or recoverable extension that can be repeated indefinitely in service.

The instrument is set to impose the desired extension and to provide a small tensioning load, then the cumulative extension is recorded for a given number of cycles or to break, and the maximum tension developed in a cycle is observed at intervals. Extensions are expressed as compound extensions based on the instantaneous length of specimen and tensions are expressed as load divided by weight per unit length of cord.

A preliminary investigation of the effect of the tensioning load, frequency of applied extension and pre-stretching, on the cumulative extension and number of cycles to break was made on cotton and viscose rayon cords. A residual tension of one kilometre weight and a frequency of 60 cycles per minute were subsequently used in measuring the cumulative extension on a range of materials, including cotton, flax, rayon, silk, nylon, wool, hair, and casein fibre. The cumulative extension is directly proportional to the logarithm of the number of cycles in many cases; a curve concave to the extension axis indicates plastic flow, whilst the opposite curvature would be produced by work hardening or stretch orientation.

It is desirable to find a measure of plasticity which will give a fair comparison of cords having different elastic moduli, and it is considered that for general purposes it is better to compare the cumulative extension for the same total imposed energy per unit mass in a given number of cycles. This is done by calculating the total imposed energy per unit mass ( $W$ ) as the sum over a given number of cycles of the product of a work factor multiplied by the imposed extension multiplied by the maximum tension developed in the cycle, and a value for the cumulative extension is interpolated from a plot of  $W$  against cumulative extension at an arbitrarily chosen value of  $W$ .

On the above basis, the cords showing least plasticity, *i.e.*, low cumulative extension, are linen, nylon, and silk, and these are followed in order by Durafl, stretched cotton cord and Fortisan. Hair, wool, high tenacity viscose (Tenasco) and unstretched cotton cord form the next group with intermediate plasticity, whilst ordinary viscose rayon, acetate rayon and casein fibre show considerable plasticity.

The cumulative extension test serves the practically important purpose of showing, sensitively, failure in recovery from oft-repeated small strains that occur in use with most materials, and can be used to screen out poor materials in the development of new fibres. It will show the effect of sizing, scouring, and lubricating treatments and the effect of varying the twist on the recovery properties of cords.

Khayatt and Chamberlain<sup>46</sup> point out that while much attention has previously been paid to the elastic properties of animal fibres as measured in extension, much less is known of the corresponding properties in flexion, mainly because the experimental determination is much more difficult. They decided to attempt to determine experimentally Young's modulus, both by extension and bending for a series of samples of hair and wool.

Parallel determinations of Young's modulus by bending and stretching at 65% R.H. and 22.2° c. have been made on fibres drawn from samples of three different types of animal fibre, and one type has additionally been examined after descaling by abrasion. The results show that in all cases the values of the modulus by bending are less, not greater, than those of the modulus by stretching; and that the effect of descaling is to reduce both moduli to approximately the same extent.

A new micro-apparatus for the determination of Young's modulus by bending, using wool fibres and human hair, is described and its use explained.

Hoffman<sup>47</sup> shows that the resiliency of a material depends on the modulus of elasticity, the extent of recovery from strain and the change of these two parameters with time. He proposes the definition "resiliency is a stress-strain-time property of a material characterising the completeness of recovery from deformation and varying in kind with the modulus of elasticity and the rate of recovery." The application of three-dimensional graphical representation is demonstrated. It is shown that four types of resiliency arise from the four permutations of high and low moduli with high and low rates of recovery, and the author argues that the extent of resiliency is the degree of recovery in a specified time, that whilst "resiliency" is a specific property of a substance "resilience" is a total property depending also on size and shape.

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# CELLULOSE AND TEXTILE CHEMISTRY

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## Cellulose

DURING the last 25 years the main features of the structure of cellulose have become well established and are now generally accepted. The cellulose molecule appears to consist of a chain of some 3000 anhydro-glucose units joined by glucoside linkages in the 1:4 position. When cellulose and its esters are dissolved in suitable solvents the chain molecules are discrete, but in the solid or fibrous form they are closely associated by means of transverse hydrogen bonds between the 3- and 6-OH groups of adjacent chains, forming a more or less crystalline network of considerable stability. The density of these transverse bonds varies from place to place within the fibre. In the "crystalline" regions the structure is a well-ordered one, the number of transverse bonds is a maximum and the penetrability of the lattice is a minimum. In the "inter-crystalline" or "amorphous" regions the density of the transverse bonds is less and the lattice is more open and more permeable to other molecules.

The individual cellulose chain molecules are of very great length (mol. wt. of the order 500,000), and may continue from one "crystalline" region to another, passing through "amorphous" regions *en route*.

The densely-packed "crystalline" regions determine the X-ray diffraction pattern of cellulose, which has been found of such great value in the deduction of its molecular architecture. The method of X-ray diffraction gives little or no information of the architecture of the amorphous regions, and attempts are being made to fill this gap in present knowledge, and to determine the "crystalline-amorphous ratio" by a variety of techniques. Though this is clearly a matter of the greatest importance, since most reactions occur in the amorphous regions of the fibre structure, no generalisation of precise validity can be expected, since the fibrous macro-molecular structures are almost undoubtedly more prone to continuous than to discontinuous variation of degree of crystallinity.

Nevertheless, during the year under review, some new experimental techniques have been brought to bear on this problem and some progress has been made. Frillette, Houle, and Mark<sup>1</sup> have made use of the hydrogen-deuterium interchange between cellulose OH groups and D<sub>2</sub>O. They find that the interchange, when cellulose is steeped in heavy water, takes place in two stages. The first stage, supposedly due to reaction in the amorphous regions of the cellulose lattice, is complete in a few minutes, whereas the second stage is, at least with native cellulose, too slow for its rate to be measured. With regenerated celluloses, where the crystallites are less impenetrable, the rate of the second stage is, although still slow, not zero. This behaviour suggests, in agreement with the results of X-ray diffraction, that the crystallites of native cellulose are impenetrable

to water. From an examination of the exchange-time curve the "accessibility" of a sample of cellulose can be determined. The results agree with those obtained by Hermans (see 1948 Report), from density measurements of cellulose samples in water. This heavy water technique seems likely to prove of the greatest possible value in the investigation of this problem.

Another means of attack on this problem has been found in the study of acid hydrolysis. The hydrolytic breakdown of the inter-crystalline or amorphous cellulose is very much more rapid than that of the crystallites. Consequently, if cellulose is drastically treated with hydrochloric acid or sulphuric acid (*e.g.*, boiling 2.5-N.H<sub>2</sub>SO<sub>4</sub>) the fibres rapidly disintegrate, giving a residue of more or less crystalline appearance, which is highly resistant to further attack. Nickerson and Habrle<sup>2</sup> have studied the glucose content of the filtrate as well as the cuprammonium viscosity and moisture regain of the residues. The viscosity attains a constant value after a time, showing the cessation of chain break-down, whereas the moisture regain passes through a minimum, indicating a removal of a hydroscopic fraction (presumably the amorphous part) of the cellulose. Similar results were obtained, whether H<sub>2</sub>SO<sub>4</sub> or HCl-FeCl<sub>3</sub> solution is used as the hydrolytic agent. The extreme resistance of the crystallites is, no doubt due to the mutually re-inforcing effect of multiple hydrogen bond linkages between adjacent chain molecules. The estimates of crystallite chain length range from 280 glucose units for cotton to 100 for rayon. These results are of the same order as the earlier results for molecular weight of cellulose obtained by the methylation-hydrolysis end-group method.

The modern view is, of course, that in native cellulose the chain-molecules are very much larger than this, and a given chain-molecule may extend its length through several crystallites.

The acid hydrolysis method has also been applied by Philipp, Nelson, and Ziifle<sup>3</sup> in an attempt to estimate the degree of crystallinity of cellulose fibres. Using hydrochloric acid solutions of three different strengths, namely 2.5, 4, and 6-N, they find that the amount of crystalline cellulose expressed as a fraction of the total cellulose varies from 0.6 to 0.8 for rayon through about 0.85 for cotton, to 0.95 for ramie. The results for rayon correlated well with X-ray diffraction patterns, ultimate elongation and moisture absorption.

Brenner, Frilette, and Mark<sup>4</sup> claim that changes in specific volume during acid-hydrolysis of cellulose indicate an increase in crystallinity, and suggest that the rupture of cellulose chains in the amorphous regions may initiate further crystallisation.

Nelson and Conrad<sup>5</sup> have attempted to improve the technique of the acid-hydrolysis method. One of the main sources of error lies in the production of humic substances which adhere to the crystalline residues. They find that although aqueous ammonia and pyridine are useful, extraction with a hot 50% aqueous solution of ethanolamine offers the best means of removing these humic substances, and they suggest revised procedures for the determination of crystallinity of cellulose. In a later paper<sup>6</sup> these authors show that grinding reduces the apparent crystallinity

of cotton fibres, but they make the interesting further observation, that, on moistening the ground samples with water, and drying, a fraction of the lost crystallinity is regained.

Jurisch,<sup>7</sup> in the course of attempts to reduce the mercerisation period in viscose manufacture, by accelerated oxidation with hydrogen peroxide, also found chain lengths of 200 to 300 glucose units to be markedly resistant to further degradation.

A critical and comparative examination of the various methods which have been proposed for the determination of the carboxyl group content of oxy-celluloses, is described in a series of papers by Davidson and Nevell.<sup>78</sup> These workers conclude that whereas certain of the proposed methods, such as alkali titration, may be suitable for oxy-celluloses of certain specific types, they are, when applied to other types of oxy-cellulose, open to serious objections. On the whole, it would appear that the balance of advantage lies with the methylene blue absorption method. The work of Davidson and Nevell serves to emphasise once again the wide disparities in behaviour that arise between oxy-celluloses prepared by the use of different oxidising agents. Whereas cellulose, apart from differences in crystallinity or degree of polymerisation, is a fairly definite chemical entity, it is very clear that "oxy-cellulose" is not.

The purely physical methods of X-ray diffraction and birefringence measurements have been used by Hermans, Hermans, Vermaas, and Weidinger<sup>8</sup> to determine the crystallinity of cellulose and to compare the orientation of the crystalline with that of the amorphous portions of laboratory-stretched viscose fibres.

Ultra-violet and infra red spectra of cellulose films before and after oxidation have been studied by Rowen, Hunt, and Plyler,<sup>9</sup> who claim that changes in the content of hydroxyl, carbonyl, and carboxyl groups can be estimated by these means.

Optical methods have also been employed in the investigation of cellulose acetate by Martin,<sup>10</sup> who studied the diffraction of light from fibres immersed in a liquid of similar refractive index (such as decahydronaphthalene). He attributed the observed diffraction effects to minute cavities, about 500  $\mu\mu$  in diameter, formed in the fibres on stretching, and investigated the conditions under which such cavities are formed. At tensions near the breaking-value, the filaments are so full of cavities as to be entirely delustrated. The distribution of cavities appears to be related to some unit of crystal structure.

Brusset<sup>11</sup> has shown by means of X-ray diffraction that the molecular structure of cellulose is retained on heating, in absence of air or moisture, up to 300° C. At still higher temperatures the structure becomes progressively more amorphous, and a fine micellar structure showing the interatomic spacing characteristic of graphite (3.6 A.) appears.

The use of the X-ray diffraction method in the evaluation of crystallinity of cellulose has been further refined by Hermans and Weidinger.<sup>12</sup> As a consequence of a searching analysis of the diffraction pattern, after allowing for minor sources of error, such as the scattering by air, which are usually neglected, they conclude that the percentage of crystalline

cellulose is  $70 \pm 2\%$  in cotton, and  $39 \pm 3\%$  in rayons. These results are in good agreement with the values deduced from moisture absorption.

Preston and Bhat<sup>13</sup> have attempted to correlate the orientation parameter derived from swelling anisotropy, with that derived from the double refraction of viscose rayon fibres. The two parameters do not agree, except for Lilienfeld rayons. The results are taken as indicating that the swelling anisotropy is determined chiefly by the skin structure, whilst the double refraction tends to be representative of the core.

Horio, Kobayashi, and Kondo,<sup>14</sup> as a result of electron microscope studies of viscose coagulated without stretching, maintain that the distribution of minute gas bubbles in the fibre must be taken into account, and that "skin" formation occurs as a result of osmotic forces, even in the absence of stretch.

Certain minor points concerning the technique of the chemical tests have been put forward in the year under review. Noll<sup>15</sup> suggests the use of a single solution for the copper number test, namely, a mixture of cupric sulphate, triethanolamine, and caustic soda, which is stable. On account of the resistance which the shorter chain molecules (D.P. < 1000) offer to further degradation, Wannow,<sup>16</sup> suggests that the exclusion of air is unnecessary for measurements of the cuprammonium viscosity of regenerated celluloses. This observation has a certain theoretical interest also, since, if substantiated, it would dispose of the theory that the resistance of short chains to further degradation is due solely to the reinforcing effect of the multiple transverse hydrogen bonding existing in the crystallites in the solid state.

Sarkar and Chatterjee<sup>17</sup> have studied the absorption of methylene blue by jute. They find it is proportional to the acid value of the fibre and sensitive to the  $p_H$  of the dye-bath. The evidence suggests the absorption is due to salt formation with structural carboxylic acid groups. The activity of the latter can be much increased by pre-treatment with dilute alkali, which is presumed to break ester linkages or lactone groupings. It does not appear that lignin is a major factor in the absorption of methylene blue. Similar conclusions were reached by Sarkar, Chatterjee, Mazumdar, and Pal<sup>18</sup> as a result of the examination of the absorption of methylene blue by twelve different vegetable fibres.

Kullgren<sup>19</sup> is of the opinion that unstabilised nitro-cellulose also contains structural acidic groups which are capable of ionic exchange with aqueous solutions. These active groups, presumably  $\text{HSO}_4$  groups, are removed by prolonged boiling in water or dilute sulphuric acid.

Petitpas<sup>20</sup> has employed X-ray diffraction in a study of the effect of gelatinising agents on the crystal structure of well-oriented nitro-cellulose, prepared from ramie fibres. He concludes that whilst ketones, acetic esters and camphor enter the crystal lattice, nitric esters do not.

Howlett and Martin,<sup>21</sup> who examined the rate of saponification of cellulose acetates, observed that maximum solubility in water occurs at an acetyl content corresponding with one acetate group per glucose residue. This is attributed to the inhibition of the formation of transverse hydrogen bonds, and is clearly paralleled by the precisely similar behaviour of the methyl ethers of cellulose.

### Protein fibres

A useful critical review of the present position of chemical research on the structure of wool has been given by Elöd and Zahn.<sup>22</sup> They point out that alkaline hydrolysis of wool is confined to the inter-crystalline chains and the micellar surfaces, for the X-ray diagram of keratin is unaffected after alkali action. They are of the opinion that cystine is not a constituent of the crystallites, but acts as a binder between them. It is concluded from ultra-centrifuge and diffusion measurements that solutions of keratin in sodium sulphide contain single peptide chains of an average molecular weight of about 10,000.<sup>23</sup> Slow degradation, with a fall in viscosity, takes place in this solution.

Harris and Brown<sup>24</sup> suggest that a more chemically stable form of wool may be produced by breaking the unstable cystine cross-link by reduction with hydrosulphite, and then coupling with alkaline dihalide or with formaldehyde so as to produce a stable  $-S-(CH_2)_n-S-$  linkage.

Menkart and Speakman<sup>25</sup> have studied the reaction of wool with mercuric acetate as a means of producing unshrinkability of wool and hair, and Lipson and Speakman<sup>26</sup> have employed the polymerisation of methyl methacrylate and vinyl cyanide within the fibre, with a similar objective.

An interesting comparative examination of the absorption of water by peptides of increasing degrees of complexity, starting with glycine itself, has been made by Mellon, Korn, and Hoover,<sup>27</sup> who find that the water absorption increases with peptide-chain-length.

Signer and Strassle<sup>28</sup> have used aqueous solutions of lithium iodide and thiocyanate as solvents for silk fibroin in attempts to determine its molecular weight by the Staudinger viscosity method. Lithium thiocyanate gives the more stable solutions. They conclude that the length of the peptide chain in silk is greater than that of the cellulose molecule in cotton, but that a marked fall occurs during degumming with hot soap solution.

Sericin has been prepared in powder form by Raunch<sup>29</sup> using a spray drier, and the properties of sericin sols have been examined. Sericin may be obtained on a large scale from silk industry waste water, and may be used as a sizing material or as a medium for bacteriological work.

A review of the present possibilities of production of synthetic protein fibres, derived either from casein or from vegetable proteins, has been given by Traill.<sup>30</sup> The importance of structural cross-linkages is emphasised and the properties of these fibres are described. He also outlines the methods of isolating the vegetable proteins and indicates the precautions necessary to produce fibres with satisfactory resistance to wet processing. The fibres are crimped, and water absorption and heat of wetting values are comparable with those of wool. In consequence, such fibres have a warm handle.

The chroming of synthetic protein fibres is protected in U.S.P. 2,426,861, their treatment with saline solutions in B.P. 593,564 and with formaldehyde in B.P. 593,928.

### Fully synthetic fibres

The polycondensation process of the nylon reaction has been closely studied by Chambret<sup>31</sup> and the viscosities of the polymers produced under

various conditions of heating are recorded. A more exhaustive investigation of the same process has been made by Coffmann, Berchet, Peterson, and Spanagel.<sup>32</sup> The fundamental principles underlying synthetic fibre structure have been usefully discussed by H. F. Mark,<sup>33</sup> and an account of end group methods for determining the molecular weight of nylon is given by Waltz and Taylor.<sup>34</sup>

The manufacture and properties of Velon, a co-polymer of  $\alpha:\alpha'$ -dichloroethylene and vinyl chloride are described by Rowland.<sup>35</sup> The production of polythene fibres having a tenacity of 4.5 g. per denier is described in B.P. 598,464. These fibres may be cross-linked by treatment with peroxides.

### Paper

Although many matters of detail have been investigated there is little of fundamental interest to record in this field. Strachan<sup>36</sup> has made, however, the interesting suggestion that the electrification occurring in the manufacture and processing of paper has its origin in piezo-electric properties of the cellulose crystallites.

Steenberg<sup>37</sup> has discussed the visco-elastic properties of paper from a fundamental point of view, whilst Cottrall<sup>38</sup> has examined the molecular mechanism of the effect of beating on paper pulp.

There are several references, *e.g.*,<sup>39</sup> to "glassine" paper, which incorporates urea-formaldehyde resin.

### Bleaching

There are no major advances to report in this field. The Hercules Powder Company<sup>40</sup> have protected a process, the first stage of which consists of a boil with water of controlled  $p_H$ , at an exceptionally high pressure (up to 135 lb. per sq. in.). The effect of kier-boiling variations upon the quality of Indian cotton has been examined in detail.<sup>41</sup>

The addition of bromide, hypobromite, or bromate to hypochlorite bleach liquors has been described in B.P. 596,132. The use of chlorite in presence of acids has been described for the bleaching of wood pulp.<sup>42</sup> Callow<sup>43</sup> has concluded that the yellowing of jute is a photochemical and not an oxidative process, and Sarkar<sup>44</sup> is of the opinion that the change does not occur in the absence of moisture.

### Dyeing

The trend towards the inclusion of the understanding of this process within the general framework of physical chemistry has continued. The view that water-soluble dyes are to be regarded primarily as electrolytes, and not necessarily as colloidal electrolytes, is gaining general acceptance. The colour ion is adsorbed by the fibre by means of hydrogen bonds or other short range forces, whereas the counter ions are only subject to the long range restraints of the electrostatic field of force. Consequently, it is permissible to regard the anions and cations of the dye and of the added electrolyte, as independent components in thermodynamic treatment of the dyeing equilibrium, in much the same way as Donnan separated the anions and cations in his classical theory of membrane equilibrium put forward in 1911. Hanson, Neale, and Stringfellow<sup>45</sup> showed, in 1935,

that the effect of added salts upon the direct dyeing of cotton, was in agreement with this view-point.

Peters and Vickerstaff<sup>46</sup> have also applied this principle to the adsorption of direct dyes on cellulose. Their theoretical treatment is carried out by the Gibbsian method, making use of the chemical potential to deduce the criteria of thermodynamic equilibrium. This mode of treatment leads to the possibility of a quantitative definition of the "affinity" of a dye as the change in standard potential which accompanies the transfer of dye from solution to fibre. The consequent problem of defining the standard states of unit activity, in the solution and in the fibre, is however, hardly yet solved. Peters and Vickerstaff also put forward certain new quantitative data for adsorption of various dyes on cellulose, which are in fair agreement with their theoretical predictions. In order to account for certain discrepancies which appear when the absorption is very small, they suggest that a small number of positively charged basic groups may exist in cotton. This is not impossible, in view of the tenacity with which traces of combined nitrogen are retained by the fibre.

Neale<sup>47</sup> has obtained independent evidence of the validity of this view-point, *i.e.*, the independent adsorption of the dye ions, by direct measurement of the membrane potentials between dyed cellulose sheet and solutions of simple salts. If  $A$  is the concentration of immobile anions in the cellulose and  $s$  the concentration of a monovalent salt in solution, the thermodynamic theory predicts a difference of electrical potential :

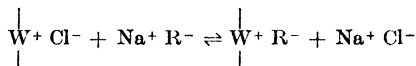
$$\psi = \frac{RT}{F} \sinh^{-1} \frac{A}{2s}$$

The experimental measurements are in good agreement with this.  $A$  consists of two parts, one (0.02 M) due to ionised carboxylic acid groups in the cellulose, and the other part representing the adsorbed dye-anions, whose amount can be found by analysis.

Fishwick and Neale<sup>48</sup> have put forward new data, self-consistent within 1%, for the absorption of the direct dye Sky Blue FF by bleached cotton, over a wide range of concentrations and temperatures. Although the plots of logarithm dye-absorption against logarithm salt-concentration or logarithm dye-concentration are linear, the slopes are in some cases inconsistent with the accepted thermodynamic theory of the dyeing equilibrium. No explanation is suggested. In a succeeding paper, Neale<sup>49</sup> shows that the absorption of two basic dyes which have direct affinity for cellulose, is in agreement with his view that cellulose carries an intrinsic negative charge in water. The initial stages of dyeing with basic dyes show a negative salt-effect, due to the diminution by salt addition of the electrostatic attraction between negatively charged cellulose and positively charged dye ions. When the amount of basic dye absorbed is sufficient to reverse the negative charge on the cellulose, the salt-effect thereafter becomes positive, as with the usual direct dyes. In normal dyeing with direct dyes, the cellulose and the colour ion both carry a charge of the same sign (negative), and the diminution of the mutual repulsion on addition of salt causes the well known positive salt effect. This point of view is not in any real sense different from the

thermodynamic treatment described, but is complementary to it. This was made clear in the work of Gilbert and Rideal,<sup>50</sup> whose equation included the electrical term in the expression for the change of thermodynamic potential accompanying dye absorption. Graham and Fromm,<sup>51</sup> working with Calcodure Blue 4 GL (C.I. No. 533), on cotton, have also found sorption isotherms of the Freundlich type. The thermodynamic treatment of the hypothesis of independent ion-adsorption (see, *e.g.*,<sup>46</sup>), leads to the prediction of a linear plot of logarithm absorption vs. logarithm concentration, and therefore, provides a theoretical basis for the hitherto empirical Freundlich isotherm, for the adsorption of electrolytes. From the temperature variation of absorption Graham and Fromm calculate the heat of absorption to be 15.2 to 22.4 kg.-cal./mol., which is very similar to Fishwick and Neale's value<sup>48</sup> (for another dye), 16.6-19.2 kg.-cal.

The combination of acid dyes with amine and amide groups in nylon fibre has been investigated by Carlene, Fern, and Vickerstaff.<sup>52</sup> These workers commenced by an examination of the titration curve of nylon with hydrochloric acid. From an examination of this curve they conclude that the amine groups combine with acid at  $p_H$ 's between 3 and 6, and thus provide ionic sites for ionic exchange with acid dye ions, as in the acid dyeing of wool.<sup>50</sup>



The amide groups react with hydrochloric acid only at  $p_H$ 's below 2, and are therefore of no importance in acid dyeing under practical conditions.

The tendering action which certain acid dyes exhibit when present at very high concentrations on wool, was also observed on nylon. Selected acid, dispersed cellulose acetate rayon and Solacet dyes were applied to undrawn nylon monofil in a range of concentration and the tensile characteristics of the dyed monofil measured. With the majority of acid and Solacet dyes (applied from acid-baths) a sharp drop in breaking load and extension occurs when the amine groups become saturated and attachment of dye to the amide group begins. Dispersed cellulose acetate rayon and Solacet dyes applied from a neutral bath at comparable concentrations cause no such degradation.

It is suggested that the development of an electrical charge on the amide groups by the adsorption of a hydrogen-ion restricts the free movement and slippage of the polymer chains and prevents their orientation when drawing is attempted. Dispersed cellulose acetate rayon dyes are presumed to be attached by hydrogen bonds to the carbonyl oxygen of the amide groups by forces comparable with those between polyamide chains. They are thus capable of being more easily displaced so that drawing can occur.

Lemin and Vickerstaff<sup>53</sup> have followed up Gilbert and Rideal's treatment of the absorption of acid dyes by wool, and have measured the "affinity" of several acid dyes and mixtures of dyes. They define the affinity of acid dyes for wool quantitatively in terms of the change in standard chemical potential of the dye during adsorption on the fibre. Equations are developed whereby the affinity can be evaluated from equilibrium

measurements of (a) the adsorption of free dye acids by wool, (b) the displacement of dye-anions from dyed wool by inorganic anions, and (c) the competition between two dyes for the sites in the wool fibre. It is shown that the equations developed for each of the three methods are valid over a wide range of  $p_H$ , dye, and salt concentrations, and that the different methods yield consistent affinity values for the six dyes which have been studied.

Marshall and Peters,<sup>54</sup> adopting the same thermodynamic treatment as Peters and Vickerstaff<sup>46</sup> have determined from new adsorption data the heats of reaction and affinities of certain direct cotton dyes on cuprammonium rayon, viscose rayon, and cotton.

Equilibrium adsorption isotherms for 14 direct dyes have been determined in the presence of sodium chloride on cuprammonium and viscose rayons, cotton, and mercerised cotton at temperatures ranging from 50° to 100° c. The standard free energy changes (of affinities) of dyeing have been calculated by the thermodynamic treatment of Peters and Vickerstaff. The treatment shows good agreement with experiment at all the temperatures investigated in the case of six dyes, agreement at the higher temperatures only with another five dyes, and poor agreement at all temperatures with the remaining three dyes. The deviations are ascribed to aggregation of the dyes in solution.

From these results, heats of dyeing and entropy changes have been calculated. The affinities and heat of reaction of any one dye are approximately the same on all four fibres. This fact supports the hypothesis that the mode of attachment of the dye to all the fibres is the same. Thus, the energetics of the process are the same and the difference in dyeing behaviour must be accounted for by purely physical differences between fibres. The results are consistent with the view that the dye is attached to the cellulose by hydrogen-bonds and the magnitude of the heats of reaction (10–30 kg.cal.) suggests that at least two such bonds are involved.

In the course of a discussion following this paper, Marshall pointed out that the suggestion made by Hanson, Neale, and Stringfellow in 1935,<sup>45</sup> that the electrical effects arising from the ionisation of carboxylic acid groups are effective in suppressing absorption of direct dyes by oxy-cellulose, may be capable of giving a quantitative as well as a qualitative explanation of this phenomenon.

Abbot, Crook, and Townend<sup>55</sup> have made a critical review of the application of dyeing theory to dyeing practice. Townend and Lemin<sup>56</sup> have examined the relation between dye-constitution and dyeing properties of damaged wool. They conclude that the complex reactivity of wool, due to amide and –S–S– linkings  $NH_2$ - groups, and physical differences between the flat surface-scale cells and spindle-shaped cortical cells, is manifested in technical processing. The most common effect, not yet adequately explained, is a loosening of the surface-scale structure which leads to complete de-scaling and renders the fibre more readily penetrated by chemicals during processing. Some treatments have a specific effect on free basic groups or introduce new acid groups, lowering the reactivity to acids. The dyeing properties of chemically treated wools are related to the simpler features of acid dye-constitution,

namely, the number and nature of the acid or acid-forming auxochromes. The chemical theory of wool dyeing is indirectly supported by these relationships.

Goodall<sup>57</sup> has emphasised the difficulties which may be caused by the presence of colloidal aggregates in wool dyeing. When using such dyes he recommends commencing at the boil in absence of Glauber's salts.

Turning now to technical dyeing practice, Wilcock<sup>58</sup> maintains that addition of  $\beta$ -naphthol is the only feasible method of controlling the dyeing of viscose rayon of uneven affinity. Level dyeing with vat-dyes presents a more difficult problem, owing to the very high affinity of the leuco-dye, but sulphate cellulose waste liquor, used with magnesium sulphate, is a useful restraining agent.

The mechanism of the after treatment process with formaldehyde, used to increase the washing fastness of direct cotton colours is the subject of discussion by Fourness<sup>59</sup> and by Whittaker.<sup>60</sup>

The interesting recent development whereby the whiteness of fabrics is improved by dyeing with ultra-violet fluorescent but colourless substances, is the subject of patents by Unilever.<sup>61</sup>

The dyeing of hydrophobic fibres, such as nylon, has received some attention. There are two general reviews of nylon-dyeing,<sup>62,63</sup> and certain new water-insoluble colours have been outlined in B.P. 595,571. The use of tetrahydrofuran and its derivatives as solvents for dyeing cellulose acetate and polyvinyl fibres has been put forward in B.P. 596,264.

Even glass fibres have not escaped the dyers' attention, and various methods of dyeing them have been described by Herbath.<sup>64</sup> These include the conversion of the fibre surface into colloidal silica by treatment with hydrofluoric acid and dilute alkali, the exchange of glass ions for coloured higher valency metal ions, and deposition of alkali soluble methyl-cellulose followed by printing or normal dyeing.

Boulton<sup>65</sup> has discussed the protection of vat-dyed fabrics against photo-degradation which is often much more severe than with undyed fibres. Drying at 100° with acid and formaldehyde or at 130° with a thiourea-formaldehyde condensate is useful for viscose fibres but is not recommended for cotton.

Egerton<sup>66</sup> records the results of a systematic investigation of the photochemical degradation of cotton dyed with vat-dyes. He finds that humidity pays a great part in promoting tendering with the "active" (yellow-orange) dyes, while oxygen is more active than air, the extent of tendering depending upon the presence of the gas; exposure in carbon dioxide or nitrogen has little effect. In presence of moisture the tendering effect varies with the concentration of dye. Exposure under moist conditions gives a similar degree of tendering on either vat-dyed or vat-pigmented cotton. The mercury vapour lamp is convenient for studying the effects of conditions on photochemical degradation, but is not an adequate substitute for sunlight in practical tests.

## Finishing

A detailed survey of the German rayon dyeing, printing and finishing industry has now been included in the B.I.O.S. reports.<sup>67</sup> On account of the prevalence of *ersatz* fabrics with low wet-strength, special devices

have been developed to facilitate the movement of fabrics without tension.

Stenters with photo-electric guiders have been devised, and speed control apparatus has been very highly developed. Most drying stoves are of the loop or brattice type working at a low temperature, and are preceded by suction devices designed to remove as much excess liquid as possible. The jig-dyeing, printing, and ageing equipment is conventional, with an exception in the case of the Gerber Ager, in which the face of the fabric does not touch the face of any roller whilst in the ager. Numerous special finishes applied to viscose staple-fibre fabrics are described in full detail. It appears that the general objective has been that of simulating as far as possible, the more desirable features of the natural fibres.

The impregnation of cellulose materials with synthetic polymers, has been further developed during the past year. MacLaren<sup>68</sup> has examined the adhesion of polymers to cellulose, and has found that there is a specific attraction between polar groups in the cellulose and polar or hydrogen-bond forming groups in the polymer.

A general review of the application of plastics in the textile industry has been given by Walter,<sup>69</sup> and Weston<sup>70</sup> has reviewed the effects of condensation resins (with special reference to Velan) on the properties of viscose-rayon. The theory of water-repellency, and laboratory methods for its determination, have been reviewed by Rowen and Gagliardi.<sup>71</sup>

A crease-resisting process for textiles involving the use of a quaternary ammonium salt of a melamine formaldehyde condensation product is protected in B.P. 587,572.

The drying of textiles has received a good deal of attention during recent years, owing to introduction of infra-red and high frequency drying as competitors with the traditional methods of steam-heated cans and hot air. Fleming,<sup>72</sup> after a careful review of both old and new methods, comes to the conclusion that the former will continue to be used for the majority of requirements, for many years to come.

### Physical testing

Doty, Aiken, and Mark<sup>73</sup> have made a study of the permeability of polymer films to water vapour. Using hydrophobic polymers such as polythene, polystyrene, and polyvinyl chloride, they find that the permeability constant towards water increases exponentially with the temperature. Increased crystallinity of the polymer decreases the permeability by increasing the energy of activation for diffusion, which is probably the energy required to open up a "hole" in the polymer lattice, into which the water molecule can enter.

Fourt and Harris<sup>74</sup> have compared the passage of water vapour by diffusion through fabrics, made of cotton, vinyon, glass, wool, and nylon with the diffusion through cellophane films and through still air. With glass and vinyon fabrics the resistance increases rapidly with the density of the fabric, indicating that the main pathway through these materials is the air space. Ordinary cotton, viscose-rayon, and wool fabrics have resistances 2 to 4 times that of air and the tightest weaving merely doubles

this. Thus appreciable amounts of water vapour must pass through the fibres themselves. This is confirmed by results obtained with viscose film through which water vapour passes rapidly. Cellulose acetate and nylon fabrics are intermediate between the above two groups. The effects of resistant fibres are most marked when the fibres occupy more than 40% of the total volume, when they occupy less the fabrics are all very similar because of the presence of air spaces of low resistance. The significance of these results with respect to the choice of clothing is discussed.

The permeability of fabrics to air under pressure has been investigated by Rainard,<sup>75</sup> who has successfully correlated his results with theoretical considerations.

A new test for water resistance of fabrics, in which the material is sprayed from the underside with water has been put forward by Skinkle and Lyra.<sup>76</sup>

Morehead<sup>77</sup> has made a useful series of direct measurements of swelling of textile fibres, by comparing cross-sections in water with those in normal heptane. He finds increases in area, expressed as a percentage of original, as follows: Silk, 19; wool, 22-26; cotton, 21; mercerised cotton, 24; ramie, 37; viscose, 44-46; acetate, 7-9; cupra rayon, 56; nylon, 1.6-3.2; vinylon, 0.2-4.3.

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## PULP AND PAPER

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*Ministry of Supply*

THE year has seen a definite improvement in the availability of raw materials and an encouraging rise in the volume of paper production. Esparto imports have exceeded the 1947 total and are back to a pre-war level. Imports of wood pulp amounted to about 1 million tons which, although also a higher figure than for the preceding year, represents only about two-thirds of the tonnage imported during 1938. Shortage of wood pulp, therefore, remains the most serious restriction on the industry. Towards the end of the year there were, however, welcome signs of some easing of the situation. Restrictions on newspaper circulation were removed and home newsprint production, which had been cut to 20% of pre-war tonnage, was, by the end of the year, increased to 45% of the pre-war figure. The quantity of waste paper collected was about 100,000 tons above the total for 1947 and, with more paper now in circulation, further improvements in the supply of this material are expected.

New developments have been seriously hampered by the difficulties and delays in securing plant and machinery, the restrictions on building, and the shortage of alkali.

In U.S.A., paper production in 1948 reached the new record total of over 22,000,000 tons. A major American development of considerable technical interest was the announcement that the International Paper Co. is to build a pulp mill in the South to produce 100,000 tons per annum of dissolving pulp, which is to be made from hard woods by a modified sulphate process.

### Raw materials

*New materials.*—Although a number of new raw materials have been investigated during the year, none holds promise of becoming of commercial importance. Thus, H. M. McKenzie<sup>1</sup> has carried out laboratory cooks on a wide variety of materials indigenous to the United Kingdom, including even thistles and nettles, without finding any of them worth further consideration—other than waste wood and cereal straws. A somewhat similar investigation has been undertaken by G. Jayme,<sup>2</sup> who subjected a large number of annual plants to sulphate cooking, and came to the conclusion that only pulps from the cereal straws were of technical and economic interest.

*Wood.*—The influence of variety, habitat and age on the chemical composition of six different varieties of poplar and on the properties of sulphate pulps made therefrom has been studied by G. Jayme.<sup>3</sup>

*Cereal straw.*—In U.S.A., the possibilities of a more extensive use of this raw material are now receiving considerable attention, notably in the investigations being carried out by S. I. Aronovsky and his colleagues of the U.S. Department of Agriculture, Northern Regional Laboratory.

Despite the fact that an enormous tonnage of wheat straw is grown in that country—it has been estimated that in 1945 the tonnage amounted to 63 million tons—it does not, at present, find any application, except in the manufacture of corrugating board.

It has been pointed out by C. J. Willard<sup>4</sup> that to leave a straw stubble after combine harvesting has a deleterious effect on subsequent crops, and the cutting of the stubble is therefore recommended for agricultural reasons. S. I. Aronovsky<sup>5</sup> emphasises the fact that the establishment of an industry based on wheat straw is dependent on the development of economical and efficient methods of collecting and handling. He proposes that the U.S. industry should standardise on a wire-bound, 80-lb. bale for which he outlines a specification. For the rapid determination of the moisture content of bales of straw—a matter of considerable practical importance—S. I. Aronovsky and H. M. Sutcliffe<sup>6</sup> recommend an electrical conductivity type instrument, with a 5-in. probe, as being practical and reliable.

For the pulping of straw, American workers are particularly impressed by the advantages of the neutral sulphite process both for making semi-cooked board pulps and for the production of bleached paper pulps.

For the production of corrugating board, G. S. Hannaway<sup>7</sup> advocates pulping with a liquor containing 1.25% sodium sulphite, 4.00% lime, and 1.25% sodium carbonate at 30 lb. per sq. in. for 8 hours. The cost of the chemicals is about 7% higher than those normally used, but this extra expense is considered to be offset by the improved rigidity of the board and by improved processing characteristics of the pulp. The experience of 15 U.S. straw-board mills with the neutral sulphite process has been summarised and commented on by B. F. Stahl.<sup>8</sup> Although the pulping procedures adopted by different mills varied greatly, it was generally agreed that to cook with sodium sulphite alone would be prohibitively expensive. The mills using sodium sulphite regularly employed it in conjunction with lime and found compensation for the rather higher chemical costs involved in the improved characteristics of the pulp, the reduction of lime troubles in the mill and the possibility of higher yields.

As already mentioned, interest in sodium sulphite cooking extends to its applications in the production of bleached paper pulps. Thus, S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson<sup>9</sup> have carried out a series of experiments in which wheat-straw was pulped by the soda, kraft, neutral sulphite, ammonia, magnesium bisulphite, and ammonium bisulphite processes. The strongest pulps were produced by the kraft, soda, and neutral sulphite processes, in that order, and the weakest by the acid sulphite processes. The highest yield of pulp was obtained by the neutral sulphite process. In a subsequent paper, S. I. Aronovsky and his co-workers<sup>10</sup> report the results of a more detailed study of the effect of the variables in the pulping of wheat straw by the neutral sulphite process. The digestion conditions recommended are to cook with 6 to 8% sodium sulphite and 2 to 4% sodium carbonate, calculated on the weight of dry straw, using a liquid to straw ratio of 7 to 1, and to boil for 2 hours at 170° C. or 4 hours at 160° C. After bleaching, using 5 to 7% total chlorine, to a brightness of 70%, the yield

of bleached pulp amounts to about 50% calculated on the weight of the dry straw.

G. Jayne<sup>11</sup> has discussed methods of hydrolysing straw, prior to alkaline cooking, in order to produce pulps sufficiently free from pentosans and ash to be suitable for the manufacture of rayon. Hydrobromic acid has a selective action in hydrolysing pentosans and by pre-hydrolysis with a mixture of hydrobromic and other mineral acids good yields of a high  $\alpha$ -cellulose straw pulp may be prepared.

According to D. E. Bloodgood and J. C. Hargleroad<sup>12</sup> chemical coagulation is too expensive a method to employ for the removal of dissolved organic matter remaining in straw-board effluent after settling. Trickle filters also proved ineffectual in dealing at a sufficient rate with wastes with the high B.O.D. figure of these effluents. In small-scale tests anaerobic decomposition was, however, found capable of effecting a very considerable reduction of B.O.D. within a reasonable time.

Analytical data, showing the effect, on the composition of Dutch cereal straws, of spring and winter sowing and of cultivation on light and heavy soils, have been published by E. L. Ritman, F. M. Muller, and J. G. Dijkhuis.<sup>13</sup>

*Other materials.*—The work carried out at the Forest Research Institute, Dehra Dun, has played an important part in establishing bamboo as a commercial raw material for pulp and paper manufacture. These investigations have been reviewed by M. P. Bhargava,<sup>14</sup> who also summarises the latest information on the pulping and paper-making properties of bamboo. One of the difficulties with bamboo is the presence of large dense nodes, resistant to the cooking process. M. P. Bhargava and C. Singh<sup>15</sup> have tried out various methods of mechanically treating bamboo (*Dendrocalamus strictus*) prior to pulping, and consider that the ideal treatment is to crush the uniformly cut stems. Bamboo has been cooked at the Herty Laboratory by the soda, sulphite and sulphate processes and the sulphate process was found to yield the strongest pulp. Contrary to Indian experience, the sulphite process was not considered satisfactory for the cooking of bamboo as it produced poor strength pulps. According to M. P. Bhargava and P. C. Batra,<sup>16</sup> the discoloration to which bleached bamboo pulps are subject can be reduced or eliminated by adopting a multi-stage bleaching process with an intermediate hot caustic soda extraction.

Chan Szu Shiang<sup>17</sup> has given an account of the application of the sulphite process to the commercial production of pulp from a tall reed, *Phragmites communis* Trin., in North China.

## Pulp production

*Wood preparation.*—A short interim report by D. C. McIntosh<sup>18</sup> gives the preliminary results of trials on the chemical killing of trees as a means of facilitating bark removal and accelerating the drying out of the timber. The tests, which cover six species of Canadian pulp-woods, have now been extended to include, in addition to ammonium sulphamate, treatment with arsenic compounds and with the sodium salt of 2 : 4-dichlorophenoxy-acetic acid. Comparisons are being made with trees which have been girdled only, without any chemical impregnation, and with trees which,

after felling in the summer, have been allowed to remain with their leaves on for varying periods. Drying out, resulting from transpiration through the leaves, at least equalled that achieved by chemical treatment. To date, the only results presented are for jack pine and aspen, but it is stated that the data for these species are typical of those being obtained respectively for the coniferous and hard wood species included in the trial. The drying of aspen was not speeded up by chemical killing. Chemically killed jack pine did, however, show an increased loss of moisture, although the season at which the treatment was applied was important.

Methods of bark removal have been reviewed by I. W. Smith,<sup>19</sup> with special reference to their suitability for the barking of slabs and edgings, a type of waste which accounts for about 30% of the volume of spruce logs entering Eastern Canadian sawmills. If bark-free, this waste could be chipped and utilised for pulp manufacture. It is concluded that small saw-mills must at present bark waste itself in a "buzzy" barker, but in larger mills (100,000 board feet per day) it would be more advantageous to bark the logs before sawing. Two barkers, the Haindl and the Waldhof machines, developed in Germany, have been described by O. Goy.<sup>20</sup>

Data for the performance of 123-in., 4-blade, whole-log chippers have been presented by D. J. MacLaurin and A. M. Van Allen.<sup>21</sup> Logs up to 26-in. in diameter, and probably up to 40 feet in length, can be fed. The equipment is said to convert 97% of the barked timber into acceptable chips and to economise in labour and material, since the waste lost in sawing the logs to an acceptable size for feeding to normal chippers is eliminated. Experience in the commercial operation of a prototype horizontal disc chipper is summarised by W. W. Brown.<sup>22</sup> Power consumption during chipping has been investigated by H. W. Rogers,<sup>23</sup> who, from an analysis of the action of the chipper, has calculated the energy theoretically required to chip a given volume of wood and has checked his conclusions against oscillograph records of measured logs of different species.

*Mechanical and semi-pulping processes.*—W. H. Montmorency<sup>24</sup> has concluded his investigations on the longitudinal grinding of wood. So far as the production of high grade ground-wood pulps is concerned this method of grinding offers no advantages and has the serious disadvantage that the percentage of rejects in the pulp is very high. Furthermore, drastic redesigning of existing equipment would be necessary before longitudinal grinding could be adopted. The rate of grinding is rather higher than with normal transverse grinding and with certain modifications the process might be of value for the production of coarse pulps for specialised purposes, e.g., building-boards.

The design of revolving disc mills and their application to the processing of various raw materials and of semi-chemical pulps have been reviewed by C. K. Textor.<sup>25</sup>

*Alkaline pulping processes.*—A systematic study of the alkaline process has been initiated at the Pulp and Paper Research Institute of Canada. The first report of this investigation, dealing with the cooking of black spruce, has been published by J. S. Hart and R. K. Strapp.<sup>26</sup> The effect

of cooking variables on pulp quality was investigated in a series of experimental digestions. It was found that if the "effective alkali" concentration was held constant, the presence of sodium sulphide in the cooking liquor had a marked effect up to 20% sulphidity; further increases in sulphidity produced a steadily diminishing effect up to 40% sulphidity, beyond which no further benefit was secured. The use of black liquor as a diluent in making up the cooking liquor was shown to be without effect on either the yield or the properties of the pulp.

Operating data and mill experience with Cottrell electrical precipitators for the collection of sodium compounds from recovery furnace gases have been summarised by L. M. Roberts, C. E. Beaver and W. H. Blessing.<sup>27</sup> The installations were found to be reliable in operation and to recover, per ton of pulp, from 88 to 145 lb. of salts of a composition which varied from mill to mill but which usually contained 75 to 85% of sodium sulphate.

A process for the pulping of beech wood, described by G. Jayme,<sup>28</sup> involves pre-hydrolysis for 2 hours with sulphuric acid, either 30% (calculated on the weight of the wood) at 70° c. or 20% sulphuric acid at 80° c. followed by a sulphate cook for 4½ to 5 hours. Furfural is obtained by the steam distillation of the acid extract. The advantages claimed for the process are a high yield of pentosan-free pulp and efficient recovery of by-product furfural.

The present uses and the potential new outlets for sulphate turpentine, which contains 50 to 60% of  $\alpha$ -pinene, 15 to 20% of  $\beta$ -pinene and 10 to 15% of monocyclic terpenes, mostly dipentene, have been reviewed by P. O. Powers.<sup>29</sup>

Tall oil, the other major by-product of sulphate pulping, continues to be the subject of investigation. The results of the monthly analysis of tall oil from a number of different mills in the Southern States of U.S.A., have been published by W. H. Jennings.<sup>30</sup> No significant seasonal difference was found in the composition of the tall oil from any particular mill, but there was a considerable variation in the results of the analysis of the tall oil from mills in different areas. W. Sandermann<sup>31</sup> states that sterols may be obtained from tall oil either by alcohol extraction of the raw sulphate soap or by the extraction of tall oil pitch. Both methods have been used on a large scale. A third method, which is claimed to enable a concentrate containing 15 to 20% of sterols to be obtained from raw tall oil with distillation, has not yet passed beyond the laboratory stage.

*Bisulphite processes.*—The technical advantages and the economics of using liquid sulphur dioxide in the preparation of calcium bisulphite cooking liquor have been discussed by E. H. Loughheed,<sup>32</sup> following the completion of a trial by a Canadian mill which used this method of acid preparation for several months. In control and ease of operation the use of liquid sulphur dioxide has advantages which should be particularly apparent during the summer months when high temperatures may give rise to troubles in acid preparation. The solubility of sulphur dioxide in calcium bisulphite solution has been determined by C. K. White, J. E. Vivian and R. P. Whitney,<sup>33</sup> who found that in the two-phase (gas, liquid) region the sulphur dioxide pressure is directly proportional

to the "true free" sulphur dioxide concentration of the solution. As the result of a number of mill trials on the Mitscherlich process pulping of spruce, W. A. Beman and H. E. Corbin<sup>34</sup> have concluded that the addition of an emulsified wetting agent, at the rate of 0.25 to 0.50 gallons per ton of chips, is not only effective in controlling pitch troubles, but, by assisting the penetration of the chips by the cooking liquor, enables rather less severe cooking to be used and improves pulp properties. L. C. Jenness and G. L. Nystrom<sup>35</sup> suggest that chip screenings can be converted into a low grade, but usable, semi-chemical pulp by a short cook, either by the calcium or the ammonium bisulphite process.

The ammonium bisulphite process has been further studied. D. E. Marriner and R. P. Whitney<sup>36</sup> have published data for the solubility of sulphur dioxide in ammonium bisulphite solution and A. E. Markham and J. L. McCarthy<sup>37</sup> have investigated the changes in composition which occur during the vacuum evaporation and steam stripping of ammonium sulphite waste liquors. Ammonia is not lost during vacuum evaporation. In a subsequent paper<sup>38</sup> these authors, in conjunction with Q. P. Peniston, reported that, by subjecting the concentrated waste to a temperature not exceeding 600° C. it is possible, under suitable conditions, to recover 90% of the ammonia present in the original waste. Recovery of sulphur as sulphur dioxide for re-conversion into cooking liquor is not practicable owing to the formation of a number of complex sulphur derivatives.

The recovery of valuable by-products from sulphite waste liquor and the development of methods of reducing the polluting character of sulphite mill effluents, continue to be the subject of numerous investigations. The Marathon Corporation in U.S.A. operates commercially a process which depends on the fractional precipitation of calcium bisulphite liquor with lime to yield, firstly, calcium sulphite, which is re-used in making cooking acid, and secondly, basic calcium lignin sulphonate, which is used as the starting material for the production of various lignin by-products. Not all the lignin is precipitable but nevertheless the polluting character of the final effluent is considerably reduced. This process has been the subject of study of M. Baum, J. W. Bard, J. R. Salvesen and G. J. Brabender,<sup>39</sup> who, in a series of experimental cooks on eastern hemlock and spruce, have followed the relationship between cooking conditions, pulp quality and lignin recovery.

An up-to-date review of the more important commercial applications of sulphite waste liquor is contained in a paper by H. F. Lewis<sup>40</sup> and developments in mills on the American Pacific coast have been described by H. K. Benson.<sup>41</sup> The utilisation of sulphite waste as a dispersant in, e.g., rubber latex compounding or the manufacture of insecticidal sprays, has been dealt with by J. R. Salvesen and W. C. Browning.<sup>42</sup> Modified lignin-sulphonates, made by controlled alkaline hydrolysis under mild oxidising conditions, gave the best results. H. S. Daniels and J. L. McCarthy<sup>43</sup> found, in preliminary experiments on the fermentation of diluted, neutralised calcium bisulphite waste liquor, with *Clostridium polyfermenticum*, that about 75% of the total reducing sugars was consumed and that the yield of butyric acid amounted to 40 to 45% by weight of the sugars converted.

The analytical methods recommended by the Canadian Pulp and Paper

Association for the analysis of sulphite waste liquor have been summarised by F. H. Yorston,<sup>44</sup> who suggests additional tests, including the determination of the percentage of reducing and fermentable sugars and of the alcohol and furfuraldehyde yields. A rapid method for the determination of the sulphate-ion content of this waste has been given by G. P. Peniston, V. F. Felicetta and J. L. McCarthy.<sup>45</sup> The procedure recommended involves cation exchange to replace calcium or magnesium, with sodium, followed by titration of the highly diluted sodium-base liquor with standard barium chloride solution. Sulphite interference is eliminated by the addition of formaldehyde before titration. K. Schwabe and E. Hahn<sup>46</sup> have separated lignin-sulphonic acid from sulphite waste into 10 fractions according to the molecular size and have found, in general, a uniform gradation of properties among them. Dialysis through regenerated cellulose film has been used to purify calcium lignin-sulphonate by N. K. Hiester, J. L. McCarthy, and H. K. Benson,<sup>47</sup> who have also determined certain physical properties of the solution of the purified material and of the sodium salt and the free acid prepared therefrom.

*Neutral sulphite processes.*—An investigation of the application of the neutral sulphite process to North American woods has been undertaken by J. N. McGovern and E. L. Keller.<sup>48</sup> When cooked with sodium sulphite buffered with sodium sulphide, black spruce, which was typical of the soft woods examined, yielded pulps which, in strength, equalled kraft pulps and, in bleachability and brightness, almost equalled acid sulphite pulps from the same wood. Nevertheless, the process has serious disadvantages. The yield of pulp obtained from this type of neutral sulphite cook was low, the cooking temperatures were higher and times longer than with kraft cooking and, in the absence of a practicable chemical recovery process, chemical consumption was very much greater than in kraft cooking. When applied to hard woods, sodium sulphite-sodium sulphide digestion gave better yields of pulps which responded well to beating and in the beaten state can attain the strength of acid sulphite spruce pulps of comparable freeness. When sodium bicarbonate is used to buffer the sodium sulphite, the process becomes very flexible, and, with jack pine, pulp yields varied between 48.4 and 78.4% according to the conditions employed. The high yield pulps were quite strong whereas pulps of similar yield made by the sulphate process were weak. In comparison with sulphate cooking, for a pulp of the same lignin content, the neutral sulphite process consumes 45% more chemical, on a sodium oxide basis.

*Bleaching.*—The response of sulphate pulp of different degrees of bleachability (Roe chlorine numbers 40 to 70) to multi-stage bleaching has been studied by H. Wenzl.<sup>49</sup> About 70% of the chlorine requirement should be met by the use of unbuffered calcium hypochlorite and chlorine. The remaining 30% is satisfied by calcium hypochlorite followed by either another calcium hypochlorite stage or by sodium chlorite or chlorine dioxide. When used thus, however, chlorine dioxide has no marked advantage over calcium hypochlorite and it is employed to better advantage as a second-stage bleach following hypochlorite or chlorine and prior to the alkaline wash.

Ordinary hypochlorite bleach techniques have hitherto not been considered to be applicable to mechanical wood pulp owing to the vigorous action on lignin. However, R. M. Kingsbury, E. S. Lewis, and F. A. Simmonds<sup>50</sup> have found that a single-stage bleach, with 10% available chlorine as hypochlorite, can be controlled if it is carried out under alkaline conditions,  $p_H$  11.0 to 11.5, at a low temperature and a density not exceeding 6%. Comparisons between this method and bleaching with 2% sodium peroxide led the authors to conclude that the hypochlorite bleach is commercially practicable, particularly for hard wood mechanical pulps. Semi-chemical pulps are another class of highly lignified material which call for special bleaching treatment. Working with an aspen semi-chemical pulp made by the neutral sulphite process (yield 77%, lignin content 12%), S. A. Trivedi, R. M. Kingsbury, and F. A. Simmonds<sup>51</sup> explored the merits of various alternatives to caustic soda as an extractant between the chlorination and the hypochlorite stages of a two-stage bleach. The most promising results were obtained by extracting with 2.5% of sodium sulphite on the weight of the pulp at 10% consistency for one hour at 60° C. Such a treatment is superior to caustic soda extraction in its effect on yield and pulp properties but is inferior in resolving shives.

A plant for the continuous, high consistency bleaching of mixtures of ground wood and sulphite pulps with sodium peroxide has been described by J. A. Lee,<sup>52</sup> and the procedure to be adopted, in order to obtain the optimum results from the sodium peroxide bleaching of different pulps, has been discussed by J. S. Reichert.<sup>53</sup>

Zinc hydrosulphite is another agent which is employed commercially for bleaching mechanical pulps. The method of application of this reagent in a newsprint mill producing 260 tons (air dry) ground wood pulp per day has been described by R. R. Ferguson,<sup>54</sup> who states that the requisite brightness of not less than 56 G.E. is attainable at a consumption of 4½ to 6 lb. of zinc hydrosulphite per ton of newsprint. After bull screening, the ground wood stock is bleached in retention chambers in which it is held for 14 minutes at a temperature of about 135° F. Corrosion remains the major trouble involved in the use of this bleaching agent.

### Paper making

*Beating.*—The special features of a “controlled flow” beater, which is said to be very economical in power consumption, have been described by L. E. Randecker.<sup>55</sup> Features of the design are that the roll does not stand in and circulate the stock, and the pulp is fed to the roll at a rate sufficient only to cover the bar edges. The application of a high speed refiner (Hydrafiner) to the preparation of a variety of different stocks has been discussed by T. Agronin.<sup>56</sup> The Hydrafiner is said to be particularly effective in developing tearing strength, and to a lesser extent tensile and bursting strength, with very little reduction in freeness but where high bursting strength is required and maintenance of freeness is not important, the Jordan is to be preferred. For the production of papers with both high tearing strength and high bursting strength, it is recommended that a combination of Hydrafiner and Jordan treatments should be employed. In an account of mill trials on the use of the Hydrafiner

in the production of high quality rag papers, H. P. Espenmiller<sup>57</sup> states that no reduction in the strength characteristics of such papers occurred and their formation was improved. A comparison between the Voith O-type refiner and a Hollander beater for the mill beating of a pulp from 18° to 72° S.R. has been undertaken by W. Müller-Rid and P. Baur,<sup>58</sup> who found that, provided consistency is carefully controlled and the throughput is not forced, the continuous Voith refiner is equivalent in its effect to the beater.

*Sizing.*—D. Price<sup>59</sup> has continued his studies of rosin sizing and has described a method for the determination of aluminium hydroxide in the size precipitate. When used under standard conditions, sizes containing from 0 to 75% free rosin all have the same sizing efficiency. The composition of the size precipitate can, therefore, vary widely without affecting the efficacy of sizing. In another paper, by the same author,<sup>60</sup> it has been shown that the reduced sizing efficiency which results from the rosin sizing of heated pulps or the heating of sized pulps cannot be explained by any change in the composition of the size precipitate.

*Loading and dyeing.*—The properties and uses of titanium dioxide in paper-making have been dealt with by A. D. Hibberd,<sup>61</sup> who has given data showing the influence of beating, sizing substance and other variables in the retention of this filler and its effect on the strength and the optical properties of the sheet.

J. Keaton<sup>62</sup> has dealt with the effects of dyeing time, electrolytes and beating on the dyeing of paper. Different classes of dyestuff behave differently. With direct colours and pure pigments, sheets from beaten pulps show at least double the colour strength of those from unbeaten pulp, whereas beating has little effect on acid colours. Basic dyestuffs behave in a manner intermediate between that of the acid and the direct dyes.

*The paper-machine.*—Information relating to the design and performance of the head-boxes used in newsprint mills in Canada and Newfoundland, has been presented by R. Fraser.<sup>63</sup> An account of the improvements introduced into the design of a new, American seven-cylinder board machine has been given by J. V. Edge.<sup>64</sup> F. Lendal<sup>65</sup> has also surveyed recent developments in cylinder board machine design, such as the Goldsmith stream flow vat and the Pusey and Jones stream flow vacuum cylinder, as a result of which modern cylinder board machines can compete in output with high-speed Fourdrinier machines.

The nature of the chemical, biological and mechanical degradation of paper-makers' felts has been discussed by E. Race,<sup>66</sup> who has also considered the measures which may be taken to reduce such deterioration. The biological degradation of wet felts can be overcome by operating with a back-water  $p_H$  not greater than 6 and preferably not greater than 5.5. Alternatively, bactericides may be added to the stock or a rot-proofed felt may be employed—but few proofings exist which are sufficiently permanent and, at the same time, free from other objections. An organic mercurial specially "fixed" to the felt probably constitutes the most promising permanent proofing.

R. Danielsen and B. Steenberg<sup>67</sup> have examined the orientation of fibres in various types of paper by measurements on paper made from stock

of which 1% had been dyed or rendered fluorescent under ultra-violet light. Orientation in the machine direction is very marked on the wire side of the sheet but less so on the felt side. Both shake and slice adjustment had little effect on orientation. Indeed, although shake improves formation it was found in certain conditions to increase the machine-direction alignment of the fibres.

The coating of paper on the machine by means of a rotogravure-off-set method is considered by G. Haywood<sup>68</sup> to have the advantage of producing a very uniform product. With a given knurled roll, the weight of coating applied was automatically maintained constant, whilst the transference of the coating to the paper, by a rubber-coated offset roll, compensated for any imperfections in the rolls.

*Slime control.*—Slime control in paper mills has been dealt with by a number of authors. The species occurring in the slime flora of British paper and board mills have been identified and described by A. G. Prendergast.<sup>69</sup> In the experience of S. Pehrson,<sup>70</sup> slime from the paper machine in a combined mechanical pulp and newsprint mill is essentially fungal in origin even when conditions are more favourable to bacteria. The main organisms occurring in this mill were *Lecytophora lignicola* Naune and *Cladosporium spp.* An account of practical mill experience in the control of slime has been given by J. Horsley,<sup>71</sup> who finds phenyl mercuric acetate effective in a mill operating on 100% waste paper, and by W. A. Wiltshire,<sup>72</sup> who prefers to arrange for the drip feeding of a 10% solution of phenyl mercuric borate in ethylene glycol. A further report on the investigations on slime control which are being carried out by the Institute of Paper Chemistry has been published by B. F. Shema, J. B. Anderson and J. W. Appling.<sup>73</sup> The installation of an improved design of slime board at strategic points in the mill is recommended as a method of observing the incidence of slime formation. In a ground wood mill it was found more effective to add an organic mercurial in single dose once per shift (i.e., every 6 hours) rather than a larger total quantity in hourly doses.

In dealing with very serious slime troubles in a Canadian pulp and paper mill making newsprint using a highly infected water supply, E. L. Neal and S. F. Jennings<sup>74</sup> found it necessary to increase the chlorination of all incoming water, including that used in the drum barkers, so as to give a residual chlorine content of 1 to 1.5 p.p.m. and to use a mixture of chlorophenates and organic mercurials in the paper mill. F. A. Soderberg<sup>75</sup> emphasises the desirability of cleaning the system from slime accumulations before instituting chemical control methods. Regular dosage with a dispersing agent is advocated as a means of ensuring freedom from agglomerations of adhesives, etc., on which slime formation occurs; also, the addition of a combination of phenyl mercury lactate, as a bactericide, and of dichlorodihydroxydiphenylmethane, as a fungicide.

C. R. Haefele<sup>76</sup> has found that the foaming troubles sometimes experienced when using sodium pentachlorophenate for slime control are dependent on the  $p_H$  of the stock and can only be avoided between  $p_H$  6 and 7. The sodium salts of other chlorophenols and of phenylphenol vary in the  $p_H$  at which they give rise to foam formation and may often

be employed when the  $p_H$  is such that pentachlorophenol would be unsuitable.

The use of highly toxic organic mercurials on a large scale naturally raises the question of the extent to which such compounds are likely to cause trouble in the mill effluent. Phenyl mercuric acetate was found by S. Vallin<sup>77</sup> to be toxic to young salmon and roach in concentrations above 0.01 to 0.02 p.p.m. According to this author, the mercurial can be removed from the effluent by precipitation with alum, an observation which is not accepted by S. O. Pehrson and N. J. Lindberg.<sup>78</sup> These latter workers found that phenyl mercuric acetate is retained by all pulps and particularly by ground wood pulp. Alum, however, reduced retention; thus, when 0.001% of phenyl mercuric acetate was added to a 2% ground wood stock 95% retention was obtained, whereas if alum was also added the retention dropped to 50%.

The physiology and morphology of iron bacteria have been described by K. Duchon and L. B. Miller.<sup>79</sup> The organism of greatest industrial importance is *Crenothrix polyspora*. Iron bacteria proved surprisingly resistant to most bactericides at economic concentrations. Treatment with chlorine or hypochlorite was considered to offer the best practical means of control.

*Wet strength paper.*—Melamine formaldehyde acid colloids have been studied by J. K. Dixon, G. L. M. Christopher, and D. J. Salley,<sup>80</sup> who conclude that the average degree of polymerisation is from 10 to 20 and that only polymers with a D.P. exceeding 4 are capable of being adsorbed on to paper fibres. The polymer in solution has a net free positive charge which decreases with age, whereas the polymer pulp adsorption complex has a positive charge which increases with the age of the polymer and eventually prevents further resin adsorption. The variation in results which have been obtained at different mills apparently carrying out the same melamine formaldehyde wet-strength process is attributed, by C. S. Maxwell and W. F. Reynolds,<sup>81</sup> to differences in the concentration of anions, particularly sulphate ions, in the mill stock to which the resin was added. Whereas cations have no significant effect and small quantities of anions are necessary to achieve optimum results, higher percentages of anions cause precipitation of the resin before it can be adsorbed. Trivalent anions have an even greater effect but are not normally present in paper mill waters, and monovalent ions are not troublesome unless present in concentrations exceeding those which are likely to be found under mill conditions. In practice therefore only sulphate ions are likely to exercise any influence. The mill procedures recommended involve the beating of the stock prior to the addition of the melamine formaldehyde resin, and the addition of the resin to the stock containing a sulphate concentration of about 75 p.p.m. (i.e., before the addition of the bulk of the alum). The stock should then be allowed to stand for at least 15 minutes.

L. Henrikson and B. Steenberg<sup>82</sup> have studied the use of urea-formaldehyde resins for the production of wet-strength paper and have come to the conclusion that the mechanism of the retention of urea resins differs from that of melamine resins and is very much more complex. Modification of urea resins by the introduction of ionogenic groups failed

to improve retention characteristics and had the disadvantage of inducing susceptibility to flocculation by electrolytes to which the ordinary urea resins were not sensitive. The degree of condensation of the resin was found to affect retention.

I. Bursztyn<sup>83</sup> has used a differential staining technique to examine microscopically the distribution of the resin in wet-strength paper and has found that, when added at the beater, both melamine-formaldehyde and urea-formaldehyde resin are deposited outside the fibres of the finished sheet. The melamine-formaldehyde was found to be uniformly distributed as small particles whereas the urea-formaldehyde occurred more irregularly as larger particles probably retained by mechanical entanglement.

In addition to its effect in conferring greatly increased wet-strength, melamine-formaldehyde resin improves the dry strength of paper. C. G. Weber, M. B. Shaw, M. J. O'Leary, and J. K. Missimer<sup>84</sup> suggest that melamine-formaldehyde should be used as a means of obtaining strength characteristics with the minimum of beating, particularly in the production of papers into which beating tends to introduce undesirable characteristics. Data for experimental offset papers showed that, by employing melamine formaldehyde resin, it was possible to produce a paper equivalent in strength and pick resistance to a well beaten paper and superior in oil-absorption, tearing strength, folding endurance and resistance to curling.

R. J. Myers and L. E. Kelly<sup>85</sup> call attention to Amberlite W-1, a neutral, water-soluble polymer of undisclosed composition, which can be cured at normal drier temperatures without the aid of acid catalysts or other agents. Exceptionally high strengths were produced, both in the wet and the dry conditions, and the wet-strength properties were permanent against prolonged exposure to water and resistant to acids, although susceptible to alkalis.

### Testing and analysis

*Pulp testing.*—A study of the variables involved in the  $\alpha$ -cellulose determination has been undertaken by A. S. O'Brien, R. C. Bloom and L. K. Reitz,<sup>86</sup> who found that the method used for the comminution of the sample was very significant and recommend that drastic grinding treatment should be avoided. Errors due to the determination of the moisture content of the pulp were eliminated by carrying out the determination on vacuum-dried material. The procedure for the dilution of the 17.5% sodium hydroxide solution prior to filtration was found to require standardisation. Methods for determining the reactivity of cellulose pulps to acetylation and xanthation have been described by G. Jayme<sup>87</sup> and the same author in collaboration with L. Rothamel<sup>88</sup> has outlined a centrifugal method for determining the swelling value of cellulose pulps.

E. Stephanson<sup>89</sup> considers the equipments in general use for the determination of the beating properties of pulps, *viz.*, the Lampen mill, the Valley beater and Jokro mill, are all subject to serious shortcomings, which he has sought to avoid in developing a new laboratory beating apparatus, the P.F.I. mill. This equipment, which is made of bronze

consists of a roll with 33 bars, which rotates in a horizontal position in a cylindrical vessel which also rotates in the same direction as the roll. The wall of the container thus constitutes a continuous bedplate for the roll. The roll revolves at 1,500 r.p.m., thereby subjecting the pulp to the action of nearly 1000 bars per second. The P.F.I. mill is designed to handle 25 grammes of pulp per charge and it beats this quantity of pulp to 80° to 95° S.R. in a few minutes.

As a means of speeding up the making of standard sheets by the British pulp evaluation technique, J. d'A. Clark<sup>90</sup> suggests that the sheets should be vacuum couched and that the pressing should be automatically controlled. It is claimed that these modifications to the official method do not seriously affect the results obtained. C. E. Hrubesky<sup>91</sup> has compared five different freeness testers and failed to find any exact correlation between the results obtained with any of them.

For the evaluation of pulps for fibre-board manufacture, H. D. Turner, J. P. Hohf and S. L. Schwartz<sup>92</sup> have developed a laboratory method which they have used to study the effect of a number of variables on the properties of fibre-board.

*Paper testing.*—B. Ivarsson<sup>93</sup> has continued the investigations on the visco-elastic properties of paper referred to in the 1947 Annual Report and has dealt with the mechanical conditioning of paper and interpretation of stress-strain curves. Studies in the rheology of paper have also been initiated in Canada and have been reported on by S. G. Mason.<sup>94</sup>

L. K. Reitz and F. J. Sillay<sup>95</sup> have applied statistical methods to a comparison of the measurement of folding endurance by the Schopper and the M.I.T. machines and have found no difference in precision between them. The effect of operational factors such as gauge calibration, pumping rate, and clamping pressure on the determination of bursting-strength by the Jumbo Mullen bursting strength tester has been dealt with by R. C. McKee, C. H. Root, and L. R. Ayers.<sup>96</sup> A chainomatic type tensile strength testing machine with photo-electric controls has been developed by B. Ivarsson and B. Steenberg.<sup>97</sup> The instrument, which measures elongation to 0.01 mm., has been employed in rheological studies.

The Bendtsen roughness tester, an instrument of the air-leak type, has been improved and standardised by C. A. Sankey and P. H. White,<sup>98</sup> who consider the instrument particularly suitable for measurements on newsprint—it is less sensitive with smoother papers. A feature of the instrument is that the air leak is measured over a distance of only 0.015-in., i.e., a distance of an order likely to affect printing surfaces.

In a very interesting paper on gloss measurement, V. G. W. Harrison<sup>99</sup> has come to the conclusion that the Ingersoll glarimeter, although probably the best of available instruments, is only suitable for rough work and mill control purposes, as it cannot always separate samples which can be visually distinguished and which differ to an extent which is of commercial importance. The results of experiments, in which a range of samples was visually graded by a large number of different observers, suggested that smoothness may unconsciously be assessed in the visual evaluation of gloss. The relation of gloss to colour has been discussed by R. S. Hunter,<sup>100</sup> who states that, for a good printing paper,

sheen, measured by the modified Oxford glarimeter, should be high and contrast gloss, determined by the Ingersoll glarimeter, low.

The Papermakers' Association, Technical Section, have issued three new test methods, namely, P.T. 14 p.m.,<sup>101</sup> "Provisional Methods for Testing the Wet-Strength of Paper," which recommends evaluation by means of the determination of wet-tensile strength using the Finch device, P.T. 15 p.m.,<sup>102</sup> "Methods for Testing the Sizing Properties of Paper," which approves as provisional standards the Cobb, the dry indicator and the potassium thiocyanate tests, and P.T. 16 p.m.,<sup>103</sup> "Provisional Absorbency Test for Bibulous Paper."

TAPPI suggested method T.479 s.m.-48,<sup>104</sup> "Printing Smoothness of Paper," covers the Bekk, the Gurley Hill, S-P-S and the Williams methods. An A.S.T.M. proposed specification<sup>105</sup> for absorbent insulating paper has also appeared.

Apparatus for the determination of the resistance of insulating board to impact and to concentrated loads has been designed by M. H. LaJoy and F. B. Rowley.<sup>106</sup> In a further paper dealing with their accelerated method for measuring the penetration of water into insulating board, W. A. Wink and J. A. Van den Akker<sup>107</sup> have shown that, by carrying out the test at a temperature of 130° F., it can be speeded up considerably, without affecting the order in which samples are graded. B. Holmgren<sup>108</sup> has critically discussed the tentative test methods under consideration by Swedish manufacturers of hard and insulating boards and has proposed certain modifications.

Experiments carried out by E. A. Behr<sup>109</sup> to determine the effectiveness of arsenic compounds and pentachlorophenates in protecting insulating board from micro-biological and termite attack have included actual tropical exposure trials involving "graveyard" tests in which samples of the board are half buried in the ground. Most promising results were obtained with copper pentachlorophenate.

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# PLASTICS

BY MEMBERS OF THE PLASTICS GROUP

## POLYMERISATION PRODUCTS (J. W. C. Crawford, B.Sc., Ph.D.)

### Polyethylene

THE emulsion polymerisation of ethylene has been described by H. Hopff.<sup>1</sup> This occurs in presence of persulphate catalyst dissolved in the water phase, with ethylene under pressure and at elevated temperature, but only if the initial reaction of the system is alkaline. Emulsifying agent is added to obtain emulsions of higher polymer content; it does not have any essential influence on the course of the polymerisation.

The polymer produced is of low molecular weight (2290) compared with normal "polythene," and always contains combined sulphur. The author considers that initiation of polymerisation commences with union of monomeric ethylene with Caro's acid; the adduct starts off the polymerisation process. The Caro's acid results from hydrolysis of the potassium persulphate catalyst. The sulphur entering into the polyethylene macromolecules appears finally as sulphuric ester or sulphonic acid, and the oxygen liberated in reaching this state is believed to react with ethylene to produce formaldehyde, which compound is always present in amount 0.6–0.7% of the weight of polymer.

Low molecular weight products accompanying the polyethylene include saturated and unsaturated alcohols above  $C_6$ , and glycols and glycolsulphuric esters. These types of compound can be visualised as resulting from chain termination of the growing polyethylene radicals, by disproportionation or by reaction of pairs of radicals respectively.

On account of its content of sulphur acids, the polymer as obtained from the emulsion is water-sensitive, and films prepared from it re-disperse in water. Hydrolytic treatment with dilute hydrochloric acid to remove the sulphur results in products which have lost this hydrophilic property and can be fabricated into sheets and films. These show mechanical properties inferior to normal polythene. Compared with the latter, the emulsion polymer has a lower melting point, is softer, and shows a wider distribution of molecular weight species.

A. T. Larson<sup>2</sup> describes a process for preparing polyethylene emulsions in which ethylene is homogeneously polymerised at high temperature and pressure under the influence of a polymerisation catalyst; thereafter, before letting the pressure down the emulsion medium (water) and emulsifying agent are introduced. The system is then let down to atmospheric pressure, to produce a permanent emulsion of the polymer. Polyethylene emulsions are of considerable interest, for example, in the finishing or coating of textiles and paper.

Technical polyethylenes are reviewed by R. B. Richards.<sup>3</sup> The commercially available polymers cover at present a molecular weight range of 12–22,000, but experimentally prepared polymers have ranged from low molecular weight greases to polymers of 50,000 average molecular

weight. The effect of crystallinity, and of the crystalline-amorphous ratio in polyethylene upon physical properties is discussed. Although the dimensions of the crystalline units in polythene are less than the wavelengths of visible light, samples of polyethylene are commonly opaque or translucent at temperatures below the transition point at which the crystalline structures disappear. This effect is considered to be due to scattering of light by oriented groups of crystallites large enough to be visible under the microscope.

The composite make-up of polyethylene is thought to be responsible for its characteristic properties—the amorphous regions contribute to the polymer's flexibility and resilience, the crystalline component gives dimensional stability, insolubility in organic solvents, and low plastic flow. Variation in conditions of polymerisation can produce variations in the proportion of crystalline polymer (estimated from X-ray diffraction, density or thermal data) between below 50 to above 90%, technical material containing about 70%.

The principal factor determining the degree of crystallinity of a polyethylene is the extent to which the macro-molecules are branched. Branching reduces crystallinity. Interpolymerisation of ethylene with other ethenoid monomers also reduces crystallinity, as does chlorination of polythene.

In spite of its hydrocarbon structure, polyethylene shows a considerable degree of reactivity with atmospheric oxygen at elevated temperatures. This affects the technically valuable properties of the polymer adversely; thus the high-temperature rolling of polyethylene in the course of processing to film, etc., can result in loss of workability (possibly by cross-linking) and, by uptake of oxygen, a marked increase in power factor.<sup>3</sup> Incorporation of antioxidants in the polymer is advocated as a means of reducing deterioration of the properties during hot processing in presence of air.

Small amounts of diphenylolpropane or dicresylolpropane,<sup>4</sup> phenyl- $\alpha$ -naphthylamine,<sup>5</sup> or  $\beta$ -thioethers of propionic esters<sup>6</sup> have been recommended for this purpose.

The flexibility combined with considerable stiffness and the low density and inertness of polyethylene have led to its application for "squeezable" bottles.<sup>7</sup> The bottles are produced by blow moulding as in the case of glass. Because of the material's unbreakability, much saving is possible in weight and tare bulk of packages.

Allied to this use is the application of polyethylene in bottle closures, in which the springiness of polythene enables it to take the place of bottle corks.<sup>8</sup>

### Polystyrene

Technically and academically styrene and polystyrene continue to attract a large share of interest. Much attention appears to have been concentrated on investigation of the substituted styrenes and on improving the technically valuable qualities of polystyrene itself. L. Schmerling<sup>9</sup> has studied the alkylation of benzene with alkyl halides or olefines in the presence of solutions of aluminium chloride in nitroparaffins, which contain the complex  $\text{AlCl}_3\text{RNO}_2$ . These solutions are soluble in benzene, the

catalyst is thus uniformly distributed throughout the liquid phase of the reaction mixture. Propylene reacts readily at room temperature with benzene containing small amounts of the complex in solution giving isopropylated benzenes; ethylene reacts less readily, and heating under pressure, with hydrogen chloride as promotor, is desirable. Catalyst is removed from the reaction products by washing out aluminium chloride with water, and nitroparaffin with alkali. Nitromethane and nitroethane give catalysts of approximately the same activity with propene; 2-nitropropene is less active.

The yields in dehydrogenation of ethylbenzene to styrene have been studied with reference to the effects of temperature and space velocity with medium activity catalysts in the temperature range 550–650°. Catalytic decomposition is considerably faster than pyrolytic.<sup>10</sup> A chemical engineering study of the process has been published by R. R. Werner and E. C. Dybdal.<sup>11</sup>

Acetophenone, passed with a primary or secondary alcohol over dehydration–dehydrogenation catalyst, yields styrene at between 200–500°.<sup>12</sup>

$\alpha$ -Methyl styrene differs from styrene in not undergoing polymerisation under the influence of peroxide catalysts; macro-molecules are formed only in interpolymerisation with other polymerisable ethenoid compounds. Interpolymers with butadiene are of especial interest. It has been observed by G. B. Bachman and R. W. Finholt<sup>13</sup> that interpolymerisation can be inhibited in cases where the  $\alpha$ -methyl styrene is substituted in the *ortho* position. This is due to a hindrance in rotation of the *iso*-propenyl group by large *ortho* substituents and is not observed with similarly substituted styrenes. Where the *ortho* group is very small (as in 2-fluoro- $\alpha$ -methyl styrene) interpolymerisation can occur.

A new method<sup>14</sup> for preparation of nuclear-substituted  $\alpha$ -methyl styrenes consists in condensing propylene chlorohydrin with substituted benzenes, using boron trifluoride–phosphorus pentoxide dehydrant. The resulting  $\beta$ -chloroisopropyl benzene is dehydrochlorinated with methanolic potash to the  $\alpha$ -methyl styrene.

The azeotropic technique used for increasing the ease of separation of styrenes from ethylbenzenes in purifying the former from the latter by fractional distillation has been applied to the case of the separation of chloro-styrene from chloro-ethyl benzene by adding either a member of a selected group of aliphatic or *cycloalkyl* alcohols,<sup>15</sup> or of a group consisting of methyl acetoacetate, butyric acid, benzaldehyde, and acetonyl acetone<sup>5</sup> whereby chloro-ethylbenzene is removed as azeotrope on fractional distillation.

The initial stages of polymerisation of styrene (below 1% conversion) have been studied by G. Goldfinger and K. E. Lauterbach,<sup>17</sup> using carefully purified monomer in presence and in absence of molecular oxygen, the polymerisations being carried out in a range of temperatures. Induction periods in the polymerisations are considered to be due to inhibiting impurities in the styrene. After treatment to remove these, the induction periods disappear whether oxygen is present or not. In the absence of oxygen, polymerisation is probably initiated by a bimolecular reaction between styrene monomer molecules. In the presence of oxygen, there

is superimposed on this form of initiation, one based on reaction between monomer and oxygen, which involves gradual consumption of the oxygen, and explains why, in its presence, the initial rate of polymerisation is higher than in oxygen-free monomer. After consumption of the oxygen the polymerisation rate becomes that of oxygen-free monomer. The oxygen-produced initial high rate decreases with the time of storage (at 4°) before polymerisation; this is put down to consumption of oxygen at the low temperature in producing oxygen-catalysed polymerisation.

It is commonly accepted that in the emulsion polymerisation of ethenoid compounds, the principal locus of reaction is the water phase, which is saturated with monomer transferred from the emulsified droplets. V. J. Frillette and W. P. Hohenstein<sup>18</sup> have measured the solubility of styrene monomer in 2% potassium oleate at 25°. In presence of excess styrene (which further raises solubility) a value of 0.88% was found, compared with 0.022% for the solubility in pure water, showing the solubilising effect on the styrene of the micellar emulsifying agent. A colorimetric method was worked out by the authors for determination of styrene monomer dissolved in the aqueous phase; this depended on measurement of intensity of the colour of manganese dioxide suspensions formed on oxidising the monomer with permanganate. The method was used to follow the course of polymerisation of styrene dissolved in potassium oleate solution without addition of polymerisation catalyst, at temperatures ranging from 70° to 118°. After an induction period, polymerisation proceeded to give an approximately linear relationship between conversion and time, followed by much tailing-off at about 50% conversion, the reason for which is unexplained. The activation energy for the initiation step, calculated from the conversion curves, was around 17 kg.cal. per mol., which is 6–11 kg.cal. lower than values obtained in bulk or solution polymerisation.

The synthesis of styrene from benzene and ethylene has now been well worked out, and the capacity for production of monomer at low cost is large—about 100,000 tons per annum in U.S.A.; cost *ca.* 8d. per pound.<sup>19</sup> From published work it is clear that development effort is being directed to improvement of the properties of technical polystyrene, a worth-while target in view of economic value of the polymer. Purification of monomer, completeness of polymerisation and increase in molecular weight marked steps in the improvement of the properties of straight polystyrene. Two American concerns now market straight polymer showing remarkably high resistance to heat distortion.<sup>20</sup>

German experience has shown that emulsion polymerisation of styrene leads to higher molecular weight products than technical homogeneous polymerisation; emulsion polymerisation in presence of small amounts of divinyl benzene gives further increase in molecular weight, whilst inter-polymerisation with acrylonitrile yields a product of high heat resistance and very high molecular weight.<sup>21</sup> Dow Chemical Co.<sup>22</sup> have found that a polymer of outstanding flexibility even at very low temperatures, with high resistance to heat without distortion (150°) may be obtained by emulsion polymerisation of styrene, followed by addition and polymerisation in the system of conjugated diolefine (butadiene). The product is different from a normal interpolymer, which is brittle at low and rubbery

at normal temperatures, or from a coagulated mixture of emulsions of the two separate polymers, which does not extrude smoothly and cracks at the surface when flexed. The butadiene polymerises much more rapidly when added to the polystyrene emulsion than under normal emulsion polymerisation conditions.

Experimental work on stretch orientation of polystyrene is extensively reported by J. Bailey.<sup>23</sup>

### Polyvinyl chloride

Information has appeared in some detail<sup>24</sup> showing the influence exerted by impurities in vinyl chloride monomer in retarding polymerisation rates and in reducing the molecular weight of the polymers. The vinyl chloride used was obtained by pyrolysis of ethylene chloride. The latter should boil within  $0.1^\circ$  of the true boiling point; trichlorethane and chlorinated propylenes must not be present. Pyrolysis of the ethylene chloride must be carried out below  $540^\circ$ ; higher temperatures lead to the production of a monomer which even after purification gives low polymerisation rate and low molecular weight polymer. The vinyl chloride must be purified by efficient fractional distillation and the proportion of lights and heavies strictly controlled, the latter to below 0.3%. Vinylacetylene has been found in the distillation residue, and its presence in the monomer is considered objectionable. Even after careful purification, increase in length of storage of the monomer before polymerisation leads to progressively longer total polymerisation times; this is connected with the formation of material of higher boiling point which has a retarding action on the polymerisation (storage is indicated as in iron vessels; it is not stated whether air is excluded).

The same authors indicate<sup>25</sup> that in aqueous emulsion polymerisation of vinyl chloride, the induction period may considerably be shortened by reducing the  $p_H$  of the aqueous phase to below 3 through addition of hydrochloric or nitric acids, rather than the sulphuric or organic acids previously used for the purpose.

D. Brundrit and S. A. D. Hickson<sup>26</sup> show that in emulsion polymerisation of vinyl chloride catalysed, for example, by persulphate, the addition of very small amounts (0.01–0.5 p.p.m.) of copper in the form, for example, of copper sulphate greatly increases the overall polymerisation rate.

Residues of peroxide catalysts remaining in polyvinyl chloride after the polymerisation process give rise to thermal instability in the polymer, shown by the appearance of colour when the material is hot-worked. G. W. Stanton<sup>27</sup> treats such peroxide-containing polymer with alcohols at above  $100^\circ$ . Peroxide reaction disappears from both polymer and alcohol; the treated polymer gives colourless mouldings. A similar heat stabilising effect is produced<sup>28</sup> by milling N-chlorinated hydantoins into the polymer. Incorporation of zinc stearate and alkaline earth (barium) stearate in vinyl chloride interpolymers gives greater resistance to heat-discoloration than either material alone.<sup>29</sup>

Mention may be made of the technique of bleaching hot-extruded or pressed polyvinyl chloride by use of nitrogen oxides, described by H. Rein and M. Dutch.<sup>30</sup>

The addition of silicates of the alkaline earths or of lead and silver to the monomer emulsion before polymerisation is claimed by C. H. Alexander<sup>31</sup> to give products of much greater electrical resistivity than polymer to which the same materials are added after polymerisation. Similarly, claims with respect to heat or light stability are made by J. J. P. Staudinger *et al.*<sup>32</sup> for lead salts, mainly of organic acids.

Substituted benzophenones are used by T. Houtman<sup>33</sup> to stabilise polyvinyl chloride against discoloration by exposure to light.

W. Birnthal<sup>34</sup> has measured the deviation from ideality of the specific volume of polyvinyl chloride plasticised with either C6-7 fatty acid ester of thiodiglycol (ED 236) or tricresyl phosphate. Up to 18 and 29% plasticiser respectively the deviation is increasingly negative, reaching minima at these points; as plasticiser content increases further, the deviation decreases until at 60% plasticiser in both cases it is zero. The differential, partial specific volume of the plasticiser in the mixes rises with increasing plasticiser from a zero-plasticiser limiting value, 7-11% lower than the specific volume of the pure plasticiser, to identify with the latter at 20 and 30% plasticiser respectively. Beyond this point the difference becomes positive until at 60% of either plasticiser the identity is again reached and maintained to 100% plasticiser. The data are explained: initially *v. d. Waals* and primary solvation forces lead to P.V.C.-plasticiser combination with reduction in volume. When this process is finished, the volume effect rapidly becomes smaller and concurrently plasticising effect more marked. The larger amount of tricresyl phosphate required to reach the above zero difference is paralleled by the larger amount of this solvent required to give equivalent plasticising effect, in comparison with E.D. 236. A similar parallelism holds with the amounts of plasticiser required to drop the resistivity of plasticised polyvinyl chloride below that of pure polymer. The above-mentioned positive difference is thought to be due to orientation effects.

H. Jones<sup>35</sup> has discussed the Leilich parallelism between the temperature-viscosity relationships of plasticisers and the temperature relationships of mechanical properties of polymers such as polyvinyl chloride plasticised with these plasticisers.

J. Delorme<sup>36</sup> has investigated the increase in viscosity of solutions of polyvinyl chloride in a range of solvents and plasticisers. Considerable differences in the effect are shown by different solvents and by polymer of different sources. The age-increase is due to formation of molecular networks which may be dispersed or their formation hindered by agitation: passage through a turbo-emulsifier practically inhibits increase in viscosity: subjection to ultrasonic vibrations is less effective.

M. S. Moulton<sup>37</sup> discusses advances in polyvinyl paste technology in Britain. These include production of pastes of suitably low viscosity for ready application in spreading machines and easy incorporation of polymer in plasticiser during paste making. Coating of fabric, *e.g.*, for upholstery, is the greatest present field of application, but slush-moulding of the paste to form flexible cast objects is an interesting development.

The hollow casting technique for moulding articles from polyvinyl chloride pastes consists in essence of filling the (metal) mould with paste, heating to gelling temperature for long enough to obtain setting-up of

a layer of paste of the required thickness on the interior walls of the mould, and pouring out the excess of ungelled paste. After a further heating of the mould to complete gelling of the residual layer of polymer, the mould is cooled and the plastic shape extracted. The flexibility of the material permits of undercutting in mould design.<sup>38</sup>

A study has been made of the adhesion of vinyl chloride-vinyl acetate interpolymer, containing varying amounts of chloride-acetate-maleic anhydride interpolymer, to regenerated cellulose film.<sup>39</sup> The adhesion, which is assumed to depend on hydrogen bonding of cellulose hydroxyls to maleic carboxyl groups, increases in a manner expressible by : adhesion =  $K(\text{CO}_2\text{H})_n$ . For a given carboxyl concentration ( $\text{CO}_2\text{H}$ ) in the adhesive, adhesion increases with temperature. Results are examined thermodynamically.

R. L. Moore<sup>40</sup> has studied the effect of fillers of different particle size on the mechanical properties of 95% vinyl chloride-acetate interpolymer. Fillers of finer particle size—*e.g.*, channel process carbon, 0.028  $\mu$ , increase the tensile strength even up to 80% volume loading; fillers of larger particle size (order of 20–30  $\mu$ ) act as diluents and the tensile strength falls away with increasing filler content; stiffness and hardness increase more with the finer fillers than the coarser. Hot tear strength and abrasion resistance are improved more by the finer fillers, although the improvement may be less continuous than in the case of tensile strength.

### Fluorine-containing polymers

Claims for the polymerisation and interpolymerisation of vinyl fluoride indicate high temperature and pressure conditions in presence of oxygen and a small proportion of acetylene, or an organic peroxy compound as catalyst.<sup>41</sup> The polymerisation of vinylidene fluoride is carried out under pressure at raised temperature, in presence of water or inert organic solvent, and in presence of oxygen, or of peroxy compound (ammonium persulphate) and bisulphite. The polymer is a tough, orientable thermoplastic, water-resistant, and heat- and light-stable, with a "sticking point" for pressed film of 145–160°.<sup>42</sup>

The fluoropropylene produced on pyrolysis of polytetrafluoroethylene has been shown to be  $\text{CF}_3\text{CF}:\text{CF}_2$ .<sup>43</sup>

Methyl  $\alpha$ -fluoroacrylate is described by L. McGinty.<sup>44</sup> The ester may be polymerised by ultraviolet light, or by heating with a catalyst.

### Acrylic polymers

The appearance of technically available  $\beta$ -propiolactone (from the union of ketene and formaldehyde) gives special interest to the synthesis from it of acrylic acid and esters, reported by T. L. Gresham and J. E. Jansen.<sup>45</sup> Another new synthesis<sup>46</sup> is from vinylidene chloride and formaldehyde in presence of sulphuric acid.

A. M. Gakhokidze<sup>47</sup> has prepared methacrylic acid by condensing acetone and ethyl formate with dry powdered potash, first at 0°, then at room temperature over 10 days, to give  $\alpha$ -hydroxyisobutyric acid (23% theory), from which methacrylic acid was prepared by dehydration by distilling with potassium bisulphate. In spite of a poor yield obtained in the present

work, the process is of interest for development because of the low cost of the reagents.

The troublesome separation of methacrylamide from the acetone cyanhydrin-sulphuric acid conversion product has been simplified by R. H. Wiley and W. E. Waddey<sup>48</sup> by neutralising the mixture with sodium carbonate, when the methacrylamide is salted out in 88% yield on the amide present.

G. V. Schulz and G. Harborth<sup>49</sup> have carried out under more accurately controlled conditions a study of the "explosive" polymerisation<sup>50</sup> of methyl methacrylate. The reaction has been studied in benzene solution as well as with pure monomer. In dilute benzene solution an overall reaction velocity of first-order form holds throughout. At higher concentrations, or with pure ester, the initially first-order reaction changes at around 25% polymer concentration, whatever the initial monomer concentration, to the accelerated "explosive" reaction. The latter has been shown to occur under strictly isothermal conditions. A plot against conversion of the ratio,  $\gamma/\gamma_0$  (ratio of velocity constant to initial velocity constant), an over-all measure of the reaction acceleration, gives a humped curve: the relationship is approximately unaffected by catalyst concentration, and little by temperature. The acceleration is due to hindering of the chain termination reaction (mutual or disproportionation) by presence of polymer, which limits diffusion of the growing chains, although monomer may still be fairly mobile. With initiation remaining fairly constant, the total effect is increase of the polymerisation reaction and formation of chains of increased length (although reduced by chain transfer from the calculated lengths). Consistent with this view is the observation that addition of an inhibitor (trinitrobenzene) which can terminate the chains greatly depresses the "explosive" reaction. The "explosive" stage is followed by a sharp check in the polymerisation process. This is due to removal of the small amount of monomer remaining (from activation rather than participation in chain growth) by adsorption on the polymer, for which it is a solvent. Completed reaction occurs when a solvent (benzene) is present, and the check point corresponds with less monomer present as the temperature rises. Both these effects support the adsorption theory.

Virtual absence of explosive polymerisation with styrene is due to comparatively easy termination of polystyrene chains: on the other hand, the cross-linked structure of polyacrylic acid<sup>51</sup> fits in with the violently explosive polymerisations observed with this substance.

The "explosive" polymerisation of methyl methacrylate has also been examined by E. Trommsdorf, H. Köhle, and P. Lagally,<sup>52</sup> who give a similar explanation to that of Schulz for the accelerated polymerisation. Trommsdorf's observations show that polymerisations of pure monomer, monomer in solution in poor solvents for the polymer, granular polymerisation and emulsion polymerisation all exhibit acceleration. This is especially marked in poor solvents. Here the growing chains precipitate<sup>53</sup> as they form and their diffusion is strongly depressed. Accordingly, the "explosive" reaction is even more marked than in pure monomer and higher molecular weight polymer results. In a suitable solvent (chloroform) the "explosive" reaction is largely eliminable, through comparatively

free diffusion of the growing chains. The use of weak inhibitor to depress the explosive reaction is also shown—sulphur being employed in this case.

Emulsion polymerisation proceeds in two ways, firstly, polymerisation of monomer dissolved in the water-phase—this process is strongly accelerated, as water precipitates the polymer—and, secondly, of monomer which swells the precipitated polymer.

Molecular weight distributions in the product from homogeneous or granular polymerisations show two maxima, corresponding to the two phases of the polymerisation reaction. The distributions in polymers from suitable solvents, or the product from homogeneous polymerisation before commencement of the "explosive" phase of the reaction show only one.

A series of acrylic and methacrylic esters, mainly of *n*-alkyl radicals, has been prepared by C. E. Rehberg and C. H. Fisher.<sup>54</sup> For the *n*-alkyl polymers, the graphs of brittle-point temperature against number of carbon atoms in the alkyl radical are of similar shape for polyacrylates and polymethacrylates, the former being lower on the temperature scale, reaching a minimum brittle-point at  $C_8$  and thereafter showing a higher brittle-point temperature; the minimum for the polymethacrylates is reached at  $C_{12}$ . The curves are linear functions of  $\log C_x$  with brittle-point temperature down to the minima. The minima probably represent incipient crystallisation (between the alkyl chains), less easily brought about in the polymethacrylates. Williams plastometer data show parallelism with the brittle-point data.

The stress cracking of polymethyl methacrylate in presence of organic solvents has been investigated by K. Matthes.<sup>55</sup> Development of cracks on wetting with acetone requires a critical elongation of the specimen. Mere traces of solvent produce cracks when the specimen is subjected to very high initial stress. The cracks can cause ultimate failure of the specimens, unlike the tougher metals where cracks appearing at low initial stresses can be neglected in subsequent application of heavy stresses. Delayed fracture of methacrylate under constant load in presence of liquid carbon tetrachloride has been examined by C. Gurney and L. Borysowski.<sup>56</sup> Delayed failure is attributed to gradual spread of cracks caused by the surrounding medium.

Treatment of the surfaces of plastics, including methacrylates, to reduce their hydrophobic nature is described by J. J. P. Staudinger and H. M. Hutchinson.<sup>57</sup> Treatment of the material with strong acids such as sulphuric acid, or exposure to the vapour of sulphur trioxide, followed by washing in water, confer hydrophilic properties on the polymer, so that water spreads over the surface instead of collecting in droplets. Dyes are adsorbed on the treated surfaces, whilst hydrophilic cements such as glue adhere to them. Marring of the surface by the treatment is corrected by subsequent hot pressing in polished moulds.

L. M. Blumenthal<sup>58</sup> has published a review of German practice in the application of polymethyl methacrylate in artificial teeth and dentures. Data are supplied on compositions and properties, including comparisons with other materials. For filling cavities or repairing fixed bridges in the mouth, where the normal high temperature cure could not be employed, the benzoyl peroxide catalyst was activated by a tertiary amine

(e.g., tri-*n*-hexylamine). Initiation locally by a hot spatula or later infra-red radiation triggered off the polymerisation, and the doughy mixture of monomer and granular polymer in the cavity cured spontaneously.

M. Hyman and P. H. Johnson<sup>59</sup> prepare  $\alpha$ -ethoxyacrylic esters from the acetals of pyruvic esters by cracking out ethanol. The methyl, ethyl, benzyl, and *cyclohexyl* esters are claimed to give hard polymers and copolymers suitable for production of optical parts. The monomers do not polymerise under conditions of thermal activation even in presence of catalysts; strong ultraviolet irradiation is used. The polymers are free from discoloration in ultraviolet light.

Alkyl esters of  $\alpha$ -cyanoacrylic ester give hard glass clear resins: they are prepared by reacting alkyl sodium cyanoacetate with alkyl chloromethyl ethers.<sup>60</sup>

A synthesis of acrylonitrile and methacrylonitrile with technical interest<sup>61</sup> consists in vapour-phase oxidation with air of allylamine or methallylamine, over a catalyst consisting of silver mirror deposited on a carrier. Yields of the order of 90% are reached: the amines are readily prepared by ammonolysis of the technically available chlorides. Whilst other practicable methods for production of acrylonitrile already exist, an alternative technical method for preparing methacrylonitrile does not appear to have been described before.

### Cross-linking polymers

Pre-treatment of the cellulose layers for contact pressure laminates with very low molecular weight urea-formaldehyde condensate improves the electrical stability of the final product, by surfacing the cellulose with a waterproof, comparatively non-polar resin film which bonds better to the contact resin of similar low polarity. The laminates thus produced are at least equal in most respects to commercial high pressure laminates.<sup>62</sup>

In a study of the polymerisation of allyl methacrylate, S. G. Cohen, D. B. Sparrow and E. R. Blount<sup>63</sup> found that gelation of the system under benzoyl peroxide catalysis at 75° occurred when 6% polymerisation had occurred, whilst by ultraviolet irradiation at 1-25° C. in presence of diacetyl or benzoyl peroxide, 19-39% was formed at this stage. Composition of the samples showed no marked differences.

Mar tests carried out on films spun on glass indicated that of a range of 29 materials, "CR 39" [poly(diallyl diethylene carbonate)] was the most mar-resistant, alkyl-modified melamine coming next.<sup>64</sup>

The tendency of cross-linking ethenoid compounds to crack up on casting in moulds is reduced by lining the moulds with soft elastic material (e.g., a butadiene inter-polymer).<sup>65</sup>

### Miscellaneous polymers

The polymerisation and interpolymerisation of acenaphthylene<sup>66</sup> using boron fluoride catalyst gives polymers of molecular weight not less than 150,000. In one example of the procedure the straight polymer did not flow under 30,000 pounds pressure at 220°. The material is useful for

impregnation of paper for capacitor dielectrics, giving low power factor and high temperature resistance. The polymers of the vinylmethyl-naphthalenes are similar in physical (electrical) properties to styrene, but have higher softening points.<sup>67</sup>

Schildknecht *et al.*<sup>68</sup> in an examination of the polymerisation of vinyl isobutyl ether show that polymers not differing essentially in degree of polymerisation or chain length may differ in physical properties according to the polymerisation catalyst used, thus boron fluoride gives an amorphous rubbery product, whilst boron fluoride-dialkyl ether complexes give a polymer which is less rubber-like and shows crystalline structure with X-rays. It is concluded that differences in the chain structure are the causes of the difference.

N-Vinylcarbazole has been synthesised by H. Otsuki *et al.*<sup>69</sup> by fusion of carbazole and potash with ethylene oxide; the N-ethylol carbazole formed is dehydrated with potash to N-vinylcarbazole. G. B. Bachman and D. D. Micucci<sup>70</sup> have prepared and carried out preliminary studies on polymerisation and interpolymerisation of a series of vinyl pyridines and quinolines. A study of vinyl halogenated thiophenes has been made by G. B. Bachman and L. V. Heisey.<sup>71</sup>

H. A. Rigby, C. J. Danby, and C. N. Hinshelwood<sup>72</sup> have examined the rubbery polymer of acetaldehyde which is formed when acetaldehyde is cooled. No polymerisation occurs above the freezing-point of the aldehyde, and supercooling of the liquid also does not give polymer, whilst cooling well below the freezing-point gives only a little polymer. It is concluded that the reaction producing the polymer occurs during the orientation of aldehyde molecules during the act of crystallisation. The polymer is unstable at ordinary temperatures regenerating acetaldehyde at least in part.

The polymerisation of methyl isopropenyl ketone in *cyclohexane* has been studied by R. N. Haward.<sup>73</sup> *Cyclohexane* is a solvent for monomer but not polymer. The rate of benzoyl peroxide catalysed reaction is greatly increased in the range 40–80% *cyclohexane* which corresponds approximately to the region where the intrinsic viscosity of the polymer reaches a maximum. The results are generally similar to those found by Norrish and Smith,<sup>53</sup> and explained by them on the basis of hindering of chain termination by precipitation of polymer. This explanation of the effect is discussed, and the conclusion reached that the diffusion effect may control the termination rate in some cases, but not in others. The nature of the monomer may have considerable bearing on what happens.

### Process studies

The kinetics of emulsion polymerisation have been examined by W. V. Smith and R. H. Ewart.<sup>74</sup> The rate of polymerisation in monomer-swollen polymer particles is considered. In the limiting case of 0.5 growing polymer free radical per polymer particle, a simple expression is derived for polymerisation rate. This case covers the possibility of high rates of polymerisation with simultaneous high molecular weights, a characteristic of this method of polymerisation, since it is possible to have a large number of particles present compared with the free radical

concentration normally present in oil phase polymerisation. The number of particles shows increase with soap concentration (3/5ths power) and with the rate of formation of free radicals (2/5ths), but should decrease with increasing rate of growth of the free radicals ( $-2/5$ ths power).

The stability of high polymeric hydrocarbons towards depolymerisation, as determined by the lowest temperature at which volatile products appear in the order polyethylene > polystyrene > polyisobutylene. A free radical mechanism for the depolymerisation process is assumed.<sup>75</sup>

High vacuum pyrolysis of polystyrene has been carried out by S. L. Madorsky and S. Straus.<sup>76</sup> Pyrolysis begins at about 350° and is almost complete at 400°. The products are: a very small proportion of gas (carbon monoxide derived from the catalyst): about half the weight of polystyrene as monomer fraction containing a little toluene and traces of ethylbenzene: about the same amount of a fraction consisting of di-, tri-, and tetramers of styrene: and a small residue of low polymer. Results are very similar to those obtained earlier by Staudinger and Steinhöfer.<sup>77</sup>

The degradation of polymethyl methacrylate has been studied by N. Grassie and H. W. Melville.<sup>78</sup> Polymer of a range of molecular weights was depolymerised in a molecular still and the percentage of depolymerisation to monomer plotted against number average molecular weight of the residue. In the initial stages of the depolymerisation there is no change in molecular weight; with low (36,000) molecular weight polymer, there is no change until 65% depolymerisation has occurred. This behaviour is what would be expected if the polymer molecules, once split, depolymerised completely to monomer. In presence of 1:4-diamino-anthraquinone, the depolymerisation can be inhibited at a quinone concentration about equimolar with the polymer. This is explained by union of the quinone with the radical endings of the depolymerising chains.

"Redox" catalyst systems—peroxide-reducer-metal (Fe, Co) systems—are discussed by W. Kern,<sup>79</sup> and by C. S. Marvel *et al.*<sup>80</sup> No complete explanation of the process is available: for any given system, all ingredients must be carefully balanced experimentally.

Quinone completely inhibits the thermal polymerisation of styrene during the period of its effectiveness: thereafter the polymerisation proceeds at the same rate as uninhibited monomer.<sup>81</sup> A product has been isolated from this system which corresponds analytically to the union of two molecules of styrene with one of quinone in a Diels-Alder type reaction. The action of quinone in inhibiting this type of polymerisation is to react in the above manner with a bimolecular diradical from styrene, the formation of which is the initial step in the polymerisation. Hydroquinone is formed by a side-reaction not connected with the initiation reaction. It has no effect on the overall rate of polymerisation. Quinone acts as a polymerisation retarder in the peroxide-catalysed polymerisation of a styrene and methyl methacrylate. Polymerisation rates in the latter case agree with the assumption that the polymer radical attacks the quinone to form an inactive radical. This disappears by interaction with other radicals present.

G. V. Schulz<sup>82</sup> has classified inhibitors according to the stages of the polymerisation process at which they are effective, using kinetic data to do so. In a comparison with antioxidants, it was concluded that whereas all of the polymerisation inhibitors examined will inhibit autoxidation, the reverse need not hold.

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# POLYCONDENSATION PRODUCTS (A. A. K. Whitehouse, M.A., A.R.I.C.)

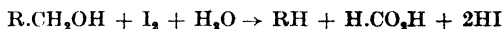
*Bakelite Limited*

## Phenolic plastics

### *Theory and structure*

RECENT work on the chemistry of phenolic resins has shown two trends. Evidence has been collected showing the comparative unimportance of ether-links in these resins, and suggestions have been made that even fully cured resins are only moderately cross-linked.

The study of the phenol-formaldehyde condensation has been helped by new methods for determining methylol groups and dibenzyl ether linkages. Lilley and Osmond show<sup>1a</sup> that methylol groups in phenol alcohols may be determined volumetrically by oxidation to formic acid with iodine.



Some substitution also occurs.

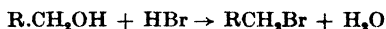


but a correction can be made for this by determining the total acid liberated iodometrically with potassium iodate and iodide solution. Owing to the nature of this correction the accuracy of the method decreases as the methylol content falls. The accuracy is about 0.5% at 30% methylol content and falls to 3% at 10% content. Below this, the errors are greater but the method is still of value for comparing the order of methylol content of a series of resins.

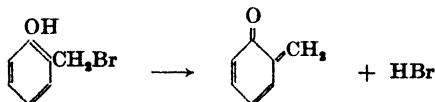
For determining dibenzyl ether linkages use is made of the Karl Fischer water-analysis reagent. This reagent has already been used by Jones<sup>2</sup> for his kinetic studies of the initial stages of the phenol formaldehyde condensation. Lilley and Osmond's method<sup>1b</sup> is to determine the water liberated on rupture of the ether links by gaseous hydrogen bromide.



A correction is made by the method given above for any methylol groups since these also liberate water.



This method is more reliable than a direct assay of the bromomethyl compound by determining its bromine content since some of these compounds decompose spontaneously to quinone-methides.

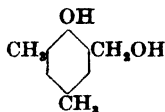


As an indication of the effect of condensation conditions on the composition of a resin some results are given for *p*-*tert*.-butylphenol resins made with a ratio of two moles of formaldehyde to one of the phenol:

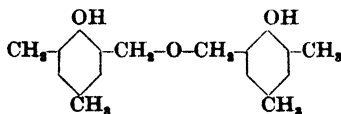
Catalyst	% CH <sub>3</sub> OH	% CH <sub>3</sub> OCH <sub>3</sub>	Molecular weight (cryoscopically)
Soda .. .. .	7.9	9.7	425
First acid, then soda .. .	11.4	1.0	544
0.7% of ammonia .. .	2.0	2.2	394
1.0% of ammonia .. .	2.9	0.5	353
3.0% of ammonia .. .	1.1	2.8	376

Lilley<sup>3</sup> has used this method for comparing the amounts of ether formation when differently substituted phenol alcohols are hardened under the same conditions. Thus saligenins with substituents *para* to the hydroxyl group were heated for several hours at 130 and 140° and it was found that the nitro-compound gave some 3–4 times as much ether linkage as the chloro-compound. This is attributed to the opposite effects of these two groups in activating the position *ortho* to the phenolic hydroxyl group. From a theoretical analysis of both the ionic and the non-ionic reaction mechanism Lilley concludes that for resols in which there are free reactive positions there is not likely to be much ether formation. The use of blocked phenol alcohols as “models” for resin formation is hence of doubtful validity, and the resins occurring in typical practice are likely to contain much less ether linkage than might be expected from such studies.

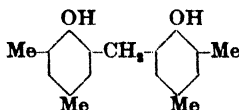
Evidence against the formation of ether-links in acid-hardened phenolic resins is provided by some calorimetric studies of Hultzs<sup>4</sup>. He measured the heat evolved in various interactions of 2,4 xylenol, its monomethylol derivate *o*-hydroxymesityl alcohol :



and the ether from the latter :



the reactions taking place at room temperature in methyl alcohol solution in the presence of *p*-toluene sulphonic acid as catalyst. The methylene bridged compound:



was formed from both the alcohol and the ether whether alone or mixed with the xylenol, with the liberation of water and/or formaldehyde. Direct reaction of the xylenol and formaldehyde also gave the same compound under these conditions. Of these several reactions, the one

between the alcohol and the xylene is most rapid and most exothermic. This work thus suggests the exclusive formation of methylene bridged structures in low-temperature acid hardening.

The second aspect of phenolic resin chemistry which has been receiving attention is that of the amount of cross-linking in hardened resins. Megson has applied<sup>5</sup> the accepted "effective radii" and valency angles of carbon to various dihydroxydiarylmethanes and shown that the chains must be very irregular with no symmetry and with varying but limited degrees of rotational freedom associated with varying degrees of brittleness. This irregularity suggests that complete cross-linking of novolak chains is not possible. This concept has been carried further by Pritchett, who suggests<sup>6</sup> that the formation of insoluble and infusible resins could be explained by a mechanical tangling and interlocking of multiple branched chain molecules. In this connection the concept of "clathrate" compounds as developed by Powell<sup>7</sup> should be noted. Clathrate compounds consist of intermeshed but independent cage-work structures. Hydrogen-bonded quinol molecules may take up such a structure and one giant "polymer" may be enmeshed by another or small molecules may be embedded without being bonded. However, reverting to phenolic resins, it would seem to the present reviewer that at least some cross-linking must occur if only because of the readiness with which phenol methylols react with any active positions in any phenolic rings.

The concept of phenolic resins as a two-phase gel-structure in which a high molecular weight phase is dispersed in a continuous low molecular weight phase has been discussed by Scheiber,<sup>8</sup> while Müller and Müller have separated these resins into fractions, compared their properties and correlated their amounts with conditions of preparation.<sup>9</sup> The fractionation was carried out by fractional precipitation of solutions in aqueous sodium hydroxide with sulphuric acid. With alkaline catalysts there was much insoluble matter already present at the cloud point showing that the low polymers keep the higher ones in solution. The proportion of the higher melting fractions was increased by increasing the sodium hydroxide catalyst concentration or by using ammonia as catalyst. This may be of direct practical value as these authors had earlier<sup>9a</sup> found that the less water-soluble and less exothermically acid hardening fractions are more successful as cold-setting adhesives. Acid catalysts give less alkali-insoluble matter, and products of a higher molecular weight for a given setting point which is said to indicate a more linear structure than that of the products of alkaline catalysis.

Some additional evidence as to the structure of phenolic resins is provided by studies of the reactions of their intermediates with other substances. Hultsch discusses<sup>10</sup> the two types of reactions involved in the combination of olefinic substances with *o*-phenol alcohols and their resins. These are, firstly, the formation of chroman rings by reaction through both the phenolic and alcoholic hydroxyls with the elimination of water, and, secondly, the loss of water between the alcoholic hydroxyl and a methylene group which is  $\alpha$ - to the olefinic group; if a phenol di-alcohol is used this second reaction may form a bridge between chains of the unsaturated compound. Other workers have studied this reaction by absorption spectra,<sup>11</sup> by observing the effects of variables on gelation,<sup>12</sup>

and by measuring the amounts of water and formaldehyde evolved under varying conditions.<sup>13</sup>

Van der Meer has experimented<sup>14</sup> with the vulcanisation of rubber by phenol di-alcohols and resols. The corresponding di(bromomethyl) derivatives are even more active. Vulcanisation is believed to proceed by way of methylene quinones formed by loss of water or hydrogen bromide. The methylene quinones then add to the  $\alpha$ -methylene groups of the rubber as in the second reaction of Hultzsch above, so that by a repetition of this reaction a bridge between chains is provided. The vulcanising ability is lost if the phenol di-alcohols are altered chemically so that methylenequinone formation is impossible, *e.g.*, by etherification or esterification. Hexamine also prevents vulcanisation with phenol formaldehyde resols, by combining with methylenequinone structures.

A somewhat related reaction is that of phenol alcohols with phenylene diamines,<sup>15</sup> forming intermediates with  $-\text{CH}_2-\text{NH}-$  links between the benzene rings, and then forming resins.

#### *Raw materials and manufacture*

Recent patented methods of obtaining phenols have included the alkylation of simple phenols with olefines,<sup>16</sup> the production of nuclearly-methylated phenols from anisole by vapour-phase treatment with activated alumina,<sup>17</sup> and the aromatisation of cyclohexanone derivatives and of isophorone in a similar manner to give phenols such as 3:5-xenol.<sup>18</sup> Details have been published<sup>19</sup> of I.G. Farbenindustrie's manufacture of phenol from benzene through the sulphonic acid and from chlorobenzene.

Favourable conditions for the vapour-phase oxidation of methanol to formaldehyde over a molybdenum oxide catalyst have been specified,<sup>20</sup> and the I.G. Farbenindustrie process in which an electrolytic silver catalyst is used has been described.<sup>21</sup> A useful source of formaldehyde for experimental work and perhaps for making resins where accurate control is important is the de-polymerisation of trioxan.<sup>22</sup> This is a first order reaction and may be carried out in aqueous or non-aqueous solvents or directly in phenol.

A kinetic study of the reaction of formaldehyde with ammonia to form hexamine has been made.<sup>23</sup>

Bettelheim and Nihlberg's study<sup>24</sup> of the manufacture of resols was mentioned in last year's review.<sup>24a</sup> It has now been translated<sup>24b</sup> and its most important contribution is on the control of resinification. During the reaction of the phenol and formaldehyde and the first part of the evaporation until a clear solution is obtained on cooling, the resin stage is unambiguously defined by one parameter such as refractive index, density or viscosity, but during the later part of the evaporation it is only wholly defined by two parameters. Hence it is not sufficient to take a fixed final viscosity; the desired final state will only be attained if the correct resin state was achieved in the reaction stage.

Details of German procedure in manufacturing phenolic resins have been published.<sup>25</sup> Bakelite Corporation has described<sup>26</sup> the preparation of the six isomeric hydroxy-hydroxy-diphenylmethanes with a view to their use for the manufacture of resins.

### *Processing*

Preheating moulding materials with live steam is so simple and effective that its use is often warranted in spite of the inferior electrical properties of mouldings made in this manner.<sup>27</sup> High frequency preheating on the other hand owes its success to its rapidity and the high quality of the products, and these two factors are such that in spite of its higher cost, its continued adoption is assured. Improvements in the apparatus have been described.<sup>28</sup>

The rolling of plastics has been considered from a theoretical point of view by Eley.<sup>29</sup> The compression stresses and temperatures observed experimentally were of the same order as the calculated values. The work required for rolling was also calculated.

For machining plastics diamond tools are recommended<sup>30</sup>; their high heat-conductivity is particularly advantageous.

Heat treatment at about 150–160° is recommended as a means of increasing the surface hardness of cast phenolic resins.<sup>31</sup>

### *Testing*

Impact strengths have continued to receive considerable attention, but no outstanding conclusions have been reached. Two papers by Frölich have become available,<sup>32</sup> one on the dynamic measurement of elasticity by causing the sample to vibrate with an interrupted air blast, resonance being observed by an electromagnetic detector; an accuracy within 1% is claimed, and the results are about 25% higher than those from static measurements. The second paper describes the measurement of hardness by observing the indentation when the test-piece is moved at a controlled rate under a pressure-loaded steel sphere. For observing the strain in transparent stressed specimens, photo-dielectric analysis has been used.<sup>33</sup>

The microscopic examination of test-pieces of phenolic mouldings is facilitated by etching with concentrated hydrogen peroxide.<sup>34</sup> Before etching the test-pieces are degreased and polished. The hydrogen peroxide acts on the cellulosic filler and shows any non-uniformities in structure. It is found in this way that high-frequency pre-heating considerably improves the uniformity of mouldings. The chemical analysis of mouldings for traces of arsenic, lead, and mercury is described in a recent British Standards Specification.<sup>35</sup>

### *Modifiers and fillers*

Modification of phenolic resins may be with a great variety of substances such as 3 : 5-xenol to increase the speed of curing,<sup>36</sup> or a fatty acid to prevent yellowing,<sup>37</sup> but perhaps the most widely used modifier is rosin. It has been proposed by Rinse<sup>38</sup> that the name "Modified Phenolic Resin" be reserved for phenolic resins modified with minor quantities of modifying agent, the name "Phenolic-Modified Ester Gum" being used for products made by heating excess of rosin with a phenolic resin and esterifying with glycerol. Some modifiers are added to give internal plasticisation. Thus elastic resins can be made<sup>39</sup> by condensing polyphenols containing two or more phenolic nuclei linked by an aliphatic

chain with formaldehyde. These polyphenols may be made by condensing simple phenols with polyolefines, low molecular weight vinyl or butadiene polymers, fatty acids or drying oils. Somewhat similar is the incorporation of novolaks in resol casting resins<sup>40</sup> in order to improve impact strength and workability.

The properties of an ideal filler and the actual properties of available fillers have been discussed by Debing.<sup>41</sup> A wide variety of agricultural residues,<sup>42</sup> including lignocellulose waste,<sup>43</sup> have been recommended. Shock-resistant mouldings can be made by using as filler portions of woven high-tenacity regenerated cellulose filaments,<sup>44</sup> or by using nylon filaments or fabric which at the same time give products with the water-resistance and good electrical properties of mineral filled materials,<sup>45</sup> in the latter case the treatment of the nylon with the phenolic resin should be carried out at a sufficiently low temperature to avoid fusion or dissolution of the nylon filaments.<sup>45a</sup>

A number of modifications in the procedure when using laminated fillers such as paper, fabric and wood-veneers have been described and patented, but there have been no major advances. A series of phenolic laminates were immersed in water and other aqueous solutions for six months by Tyrie<sup>46</sup> and tested for weight and dimensional changes and strength losses. Cotton fabric laminates showed the best resistance to alkaline conditions. In strongly acid solutions all the laminates showed serious strength losses.

### *Applications*

Phenolic resins in various forms are widely used as adhesives, and several reviews of this field have been published.<sup>47</sup> Complex compositions of a rubber, drying oil, and alkylphenol-formaldehyde resin may be used,<sup>48</sup> but simple resols are often employed as, for example, in the assembly of aircraft, for which cold-setting resols catalysed by *p*-toluene sulphonic acid were used in Germany.<sup>49</sup> When using the highly reactive resorcinol resins, a stable formaldehyde-deficient syrup may first be prepared and then hardened with more formaldehyde and alkali,<sup>50</sup> or with paraform and an alkaline earth.<sup>51</sup> Alternatively, resorcinol may be added to a monohydric phenol resol,<sup>52</sup> or an anhydrous acid-condensed resorcinol-paraform resin may be mixed in alcohol solution with polyvinyl acetate.<sup>53</sup> The use of an adhesive containing several types of chemical group is often advantageous in bonding surfaces of widely different polarities. Thus light metals may be bonded to rubbers with polyvinylbutyral-resorcinol-formaldehyde compositions,<sup>54</sup> and polyamides may be used for bonding cellulose nitrate to hardened phenolic resins.<sup>55</sup>

Ion-exchange resins are becoming of increasing importance. Cation-exchange resins usually consist of sulphonated polyhydroxyphenol-formaldehyde resins, and Bhatnagar finds<sup>56</sup> that catechol gives a more reactive resin than resorcinol. Recent suggestions for improving manufacture include condensation in the presence of a substance which forms a gel with formaldehyde,<sup>57</sup> sulphonation after partial condensation with formaldehyde,<sup>58</sup> and preparation in the presence of a solvent until gelation occurs so that a highly porous infusible mass results.<sup>59</sup> New uses are continually being found for these resins, for example, for the purification

of fruit juices and of formalin.<sup>60</sup> A useful review of applications has been given by Davies,<sup>61</sup> who has himself worked on their use as catalysts. A process was operated in Germany involving their use in this manner as ester interchange catalysts in the continuous preparation of dibutyl adipate from dimethyl adipate and butanol. The kinetics of esterification with cation-exchange catalysts have been studied by Levesque and Craig,<sup>12</sup> while Kunin and Myers<sup>63</sup> have examined the kinetics of anion-exchange. Heymann and O'Donnell discuss<sup>64</sup> whether anion-exchange resins function by true ion-exchange or by acid absorption and conclude that there is no experimental means of distinction.

### Furan resins

The basic reactions involved in the formation of resins from furfuraldehyde have been summarised by Norton.<sup>65</sup> The reactions are aldehyde condensations with phenols, the formation of high polymers through ether links or by methylene bridging, and addition polymerisation through the furan conjugated ring structure. Furfuryl alcohol may be resinified with an acid catalyst, and the resin formation and hardening stages can be separated.<sup>66</sup> The products are resistant to oil, petrol, salt water and steam. Phenol-furfural resins have been used for making paper-base laminates.<sup>67</sup> These are darker in colour than cresylic laminates and have similar electrical and mechanical properties.

### Thiophen resins

Novolak resins similar to those from phenol and formaldehyde have recently been prepared by Caesar and Sachanen<sup>68</sup> by the acid condensation of thiophen with formaldehyde. These resins cannot be thermoset with alkali and will only harden on prolonged heating at 150° with hexamine. If, however, mixtures of thiophen and phenol in the proportion of 3 : 2 are condensed with formaldehyde, resins are obtained which are suitable for use in moulding materials and can be made to set in one minute at 150°. The properties are not outstanding but impact strengths are moderately good.

### Urea-formaldehyde resins

Once again there has been very little published work on the chemistry of the urea aldehyde condensation. The Karl Fischer technique of water estimation has been applied by Kittel<sup>69a</sup> to the self-condensation of pure methylol and dimethylol urea which lost respectively 1.0 and 1.6 mols. of water per mol. This difference in water loss enables an estimate to be made of the amount of each intermediate formed during the urea paraformaldehyde condensation. The condensation is found to be influenced catalytically by the water present.

The same author has studied<sup>69b</sup> the quantitative degradation of amino-plastics and finds that acid hydrolysis followed by treatment with dimedon and acetic acid is a satisfactory method of determining the formaldehyde combined in the resin. Polymethyleneurea resins have also been degraded by heating with formaldehyde and an acid catalyst<sup>70</sup>; breakdown was found to be more dependent on the catalyst concentration than on the amount of formaldehyde used.

There have been several patents concerned with the details of the manufacture and processing of urea resins. The importance of  $p_H$  control is well known, and in one case<sup>71</sup> a borate boric acid buffer mixture is used. For measuring  $p_H$ , indicators are preferable to glass electrodes, as the latter induce surface condensation and are, therefore, unsatisfactory.<sup>72</sup> After condensation to an aqueous syrup the water may be removed by spray drying.<sup>73</sup> The powdered resin so obtained may be dry-mixed with the other moulding powder ingredients. By mechanical working on hot rolls with water it gives<sup>74a</sup> a readily flowable mass which can be stored for long periods before moulding, or the powdered resin may be converted to a more coarsely granular form<sup>74b</sup> by preheating and then passing through differential rolls at a lower temperature giving a loosely compacted sheet which may be easily granulated.

The British Standards Institute have made recommendations<sup>75</sup> for procedure in testing amino-plastic moulding materials and mouldings.

A number of publications deal with the control of the cure of urea resins. In bonding laminated structures with these resins it has been suggested<sup>76</sup> that carbon black be used as a filler and an electric current passed to generate sufficient heat to set the assembly while held in a press. Since acid-hardening adhesives tend to cure prematurely in the presence of catalysts, substances were used which are only potentially acid. The ammonium salts of strong acids have a somewhat latent action only becoming effective as the ammonia is absorbed by available formaldehyde in the resin. Even more effective is a dry mixture of such an ammonium salt with the resin and a less than equivalent amount of magnesium or zinc oxide.<sup>77</sup> This is quite stable until mixed with water, when it forms an adhesive with further delayed hardening properties. Substances which only become acid at raised temperatures are valuable hardeners; examples are silicates, chlorosilanes,<sup>78</sup> ethyl ammonium phosphates,<sup>79</sup> N-acylimides, and sulphonacylamides<sup>80</sup>; the first two of these materials may be applied to glass fibres, with subsequent application of a urea-formaldehyde resin.

The use of a urea-formaldehyde polycondensate "Uraform" as a slow acting nitrogen fertiliser was mentioned in last year's Annual Reports.<sup>81</sup> This use was protected by a patent by Rohner and Wood.<sup>82</sup> Some independent work on the same application has now been published by Clark, Lee, and Love, of the U.S. Department of Agriculture.<sup>83</sup> These authors describe insoluble nitrogen fertilisers containing 36-38% nitrogen and 4% moisture. They are much less soluble than other types of nitrogen fertilisers. The effects of mole ratio, acidity, concentration, and reaction temperature and time were examined, and it was found that the lower the mole ratio of urea to formaldehyde the lower the rate of availability of the nitrogen to the plant; in all cases, however, this mole ratio must exceed one, in contrast with the procedure for making resins.

### Melamine-formaldehyde resins

Interest in the manufacture and applications of aminotriazine-aldehyde resins has been considerable, the most important type being the melamine formaldehyde resins.

Melamine is usually made from dicyanodiamide and ammonia, but can be made by heating urea and ammonia under pressure.<sup>86,11</sup>

Moulding materials were made in Germany<sup>72</sup> by condensing equimolar amounts of urea and melamine with formaldehyde in the presence of aqueous ammonia and active carbon at  $p_H = 7$ . Glues were made from melamine and a threefold molar excess of formaldehyde, followed by milling of the dried resin with starch and wood-meal until it contained 18% of melamine and 12% of formaldehyde; this partly degraded resin mixture, when mixed with water, hardened at 100° without added hardeners.

Resins can also be made from dicyanodiamide and formaldehyde,<sup>86</sup> and from a variety of complex derivatives of melamine. The formation of resins from melamine takes place through crystallisable methylol derivatives which condense to soluble or dispersible resins and finally to hard insoluble infusible products.<sup>87</sup> Trimethylolmelamine behaves in solution as a weak base; its viscosity gradually increases as polycondensation occurs with loss of water and formaldehyde; this process has been studied by a variety of physicochemical methods.<sup>88</sup>

Melamine resins are used for increasing the wet strength of papers. They do this by increasing the inter-fibre adhesion,<sup>89</sup> probably by forming ether linkages with the cellulose.<sup>90</sup> Other uses for melamine resins are for moulding, for improving the water-resistance of starch adhesives, and as ion-exchange resins. An extensive study of the curing of melamine plywood adhesives in high-frequency fields has been made by Stoeger.<sup>91</sup>

## Polyesters

Polyester formation provides a typical example of a polycondensation reaction. Such reactions<sup>92</sup> obey the law of mass action in contrast with the more complex polymerisation reactions. Because of the relative simplicity of the process of formation of polyesters, they are often used for general studies of macro-molecular compounds. Baker's paper<sup>93</sup> on the cross-linking of polyesters such as polyundecoates by free radicals was mentioned in last year's Annual Reports. Saturated linear polyesters are gelled and thermoset by heating with small amounts of peroxides, probably by linking through methylene groups which are  $\alpha$ - to the ester group. These groups appear to be converted to free radicals by losing a hydrogen atom to the free radicals from the peroxide, and two such groups then link together. The thermoset systems in many cases retain their micro-crystallinity. When polyundecoates are heated with smaller quantities of benzoyl peroxide than are necessary for gelation, both melt-viscosity and more especially intrinsic viscosity, increase, presumably because of branching, but without the network formation necessary for gelation. However, it is found that a plot of precipitability against dilute solution viscosity still gives the same curve as for the original linear polyesters, showing that branching does not affect this relationship. Staudinger and Berndt<sup>94</sup> fractionated polyhydroxydecoic acid and polyhydroxyundecoic acid and then determined molecular weights on the fractions by osmotic pressure measurements and by determination of carboxyl and hydroxyl end-groups; they also measured intrinsic viscosities. In many cases agreement was good, while in some cases the viscosity

values were lower than expected. The authors attributed this to chain-branching. However, Schaeffen and Flory<sup>95</sup> have synthesised a series of branched chain-polymers and found that the intrinsic viscosity is only decreased by the amount of branching when this is large and then only to a small extent. Consequently, it is concluded that the deviation of intrinsic viscosity from the value expected for a linear polymer, cannot be used as a direct measure of the degree of branching.

Simple unmodified polyesters are of little commercial importance at present, but the highly crystalline polymers of ethylene glycol and terephthalic acid should soon appear in commerce as "Terylene." Since Whinfield and Dickson's first patent,<sup>96</sup> applied for in 1941, and describing the preparation of polyethylene terephthalate by ester interchange from the glycol and methyl terephthalate, several other patents have appeared. These have described the use of glycol esters<sup>97a</sup> and of terephthalic acid halides or amine salts in place of the esters<sup>97b</sup> for the interchange reaction.

During processing of the polyethylene terephthalate some degradation occurs, and it is found<sup>98</sup> that this can be reduced to less than 20% by thorough drying of the polyester until its water content is less than 0.005 mols. per repeating polyester unit. An account of the early development of polyethylene terephthalate, including the preparation of the terephthalic acid from *p*-cymene has recently been given by Hardy,<sup>99</sup> who first prepared moderate quantities in metal apparatus in the period 1942-44.

The only industrially important linear polyesters are the unsaturated polyesters which are co-polymerised with cross-linking monomers. Several reviews of this type of product have been published.<sup>100</sup> They are particularly used for "contact" and low-pressure laminating which become possible by virtue of cure taking place without the liberation of any volatile by-products. The mixture of unsaturated polyester and monomer is caused to polymerise by a peroxide such as benzoyl peroxide and this co-polymerisation can be facilitated by adding small amounts of diamines<sup>101</sup> or mercaptans.<sup>102</sup> Continuous fabric laminates<sup>103</sup> and non-planar formed sections<sup>104</sup> are made from these resins.

### Polyamides

Several papers by Korshak and Rafikov on the polycondensation of diamines and dicarboxylic acids have been reviewed in recent years. More papers in this series have now become available.<sup>105</sup> The preparation of the dicarboxylic acid and diamine raw materials and their interaction to form monomeric salts are described.<sup>105a</sup> The polycondensation of such salts as hexamethylene-diammonium adipate was carried out in xylene for 6 hours at 230° in an atmosphere of nitrogen. The water formed should be removed by a rapid current of nitrogen and the use of vacuum as the reaction is reversible.<sup>105b</sup> Equimolar proportions of the acid and amine give the highest degree of polycondensation as an excess of either component tends to block the ends of the chains.<sup>105c</sup> The polymers are stable when heated with water, or water and a phenol at 170°, but some hydrolysis occurs above 200°. This reaction may be used for recovering scrap polyamides.<sup>106</sup> With hydrochloric acid, some hydrolysis occurs<sup>105a</sup> at 100° in 6 hours, and complete hydrolysis occurs in 4 hours at 200°

under pressure. The hexamethylene diamine set free may be determined gravimetrically as its dibenzoyl derivative.

Cross-linked polyamides are formed<sup>108a</sup> by heating the linear polymers at 260° in the presence of traces of oxygen. They soften but do not melt, and they swell in hot phenols, but do not dissolve, and they cannot be drawn into filaments. They can be reconverted to soluble polymers by heating at 100° for 5 hours with hydrochloric acid.

Chambret<sup>107</sup> found that higher molecular weight polyamides could be obtained from hexamethylene-diammonium adipate by heating at 250° under vacuum than by reaction at 205°. Temperatures as high as 275° were used by I.G. Farbenindustrie.<sup>112</sup> Using this same salt and also the sebacate and  $\epsilon$ -aminocaproic acid and various mixtures of these Catlin, Czerwin, and Wiley<sup>108</sup> have found wide variations in the elastic modulus, softening point and solubility of the polyamides obtained. The polymers with lower crystallinity usually had lower softening points. Coffman and co-workers<sup>109</sup> conclude after an extensive study that polymeric hexamethylene-adipamide is of exceptional value amongst other polyamides as a fibre. They control the degree of polymerisation by using a slight excess of either acid or amine or by introducing a mono-functional acid. Hanford and Joyce<sup>110</sup> have also used acetic acid as an end-group stabiliser. They find that the polycondensation or polymerisation of  $\epsilon$ -aminocaprolactam is promoted by heating under pressure with water, and that the reaction is complete in 1-2 hours at 285°. This lactam was synthesised<sup>111</sup> in Germany during the recent war by the sequence: phenol, cyclohexanol, cyclohexanone, its oxime, caprolactam; and it was polymerised by heating under pressure. Such polyamides are said<sup>112</sup> to be easier to make and softer than those from adipic acid and hexamethylenediamine.

Amongst the many suggested modifications in polyamide manufacture there may be mentioned treatment of the polymer with formaldehyde and an alcohol, forming N-alkoxymethyl derivatives. This has been claimed<sup>113</sup> as a means of increasing the viscosity, while treatment<sup>112</sup> on rolls with paraformaldehyde or di- or tri-isocyanates has been used for cross-linking polyamides used as artificial leathers so raising their melting point and increasing their water resistance. Sulphonamide plasticisers were used in these leather substitutes.

Substitution of the hydrogen by alkyl groups on the nitrogen atoms of polyamides reduces hydrogen bonding between the chains and largely destroys the crystalline structure.<sup>114</sup> This method has been used for producing polyamides with high elasticity.<sup>115</sup> By increasing the size and number of the N-substituent groups a continuous variation in properties takes place from hard, tough, high-melting unsubstituted polyamides to soft tacky low-melting products, with long range elasticity being developed in the intermediate materials.

The molecular weights of polyamides have been studied by Staudinger and Schnell,<sup>116</sup> who found agreement between end-group and viscosity measurements for polyaminocaproic acids, which they claim indicates unbranched chain molecules.

Taylor<sup>117</sup> has found the relation  $M_n = 1300 [\eta]^{1.39}$  to hold for polycondensates of hexamethylene-diammonium adipate with molecular

weights in the range 2500–5000. The amine end-groups were determined<sup>118</sup> by conductimetric titration in aqueous phenol alcohol mixtures, while the carboxyl end-groups were determined by dissolving the polymer in benzyl alcohol at 175° and titrating with caustic potash using phenolphthalein as indicator. Taylor has also<sup>117</sup> fractionated polyhexamethylene-adipamide in a phenol-water two-phase system at 70°. The molecular weight distribution data confirm the assumption that the reactivity of a functional group is independent of the size of the molecule to which it is attached.

In addition to the many uses of nylon in filament form it has been used as an adhesive for sealing tape,<sup>119</sup> as a leather substitute in Germany with sulphonamide plasticisers,<sup>72</sup> as a moulding material,<sup>120</sup> and in film form. Films were made in Germany from solutions of mixed polyamides<sup>121</sup> for use for anti-gas protection, while nylon films have recently been shown in this country to be of value as surgical dressings<sup>122</sup> because they are permeable to water vapour but impermeable to micro-organisms.

### Silicones

A valuable review of the silicones by Hardy and Megson<sup>123</sup> covers their history, chemistry, and industrial significance. The preparation of the chlorosilane intermediates, *e.g.*,  $\text{SiMe}_2\text{Cl}_2$ , is by a Grignard reaction from silicon tetrachloride,<sup>124</sup> or by direct reaction of alkyl halides with silicon<sup>125</sup> or the high temperature reaction of silicon tetrachloride with paraffins may be used.<sup>126</sup> These chlorosilanes are difficult to separate owing to the closeness of their boiling points. One method is to form the chloroethoxysilanes with ethylene oxide, separate these by fractional distillation, and hydrolyse directly to silicones or regenerate the chlorosilanes with an acid chloride.<sup>127</sup> A second method is by azeotropic distillation with aceto- or acrylonitrile.<sup>128</sup> Alternative intermediates to the chlorosilanes are the more stable ethoxysilanes, *e.g.*,  $\text{SiMe}_2(\text{OEt})_2$ , which may be made from ethyl silicate and a Grignard reagent.

Silicone resins are formed by hydrolysing the chloro- or ethoxy-silanes, and hydrated salts or metal hydroxides have been suggested<sup>129</sup> for carrying out the hydrolysis. Mixtures of aliphatic and aromatic silanes may advantageously be used.<sup>130</sup> The linear polysiloxanes may be stabilised by adding an organic amine,<sup>131</sup> or cured by heating with metallic driers.<sup>132</sup> In order to avoid the disadvantages of the liberation of water during cure, silicones can be made by the hydrolysis of allyl or vinyl silanes and then cured by polymerisation.<sup>133</sup>

The determination of silicon contents can be carried out by fusion of samples with sodium peroxide and sugar in a nickel Parr bomb, conversion of the silicon to silicomolybdic acid and estimation with 8-hydroxy-quinoline.<sup>134</sup>

For an outline of the uses of silicones as fluids, lubricants, greases, resins, rubbers, and agents for imparting water-repellency reference should be made to Hardy and Megson's review.<sup>123</sup> One of the largest scale uses is as a dielectric grease for ignition sealing and preventing corona discharge in aircraft engines.<sup>135</sup> Silicones are very suitable for this application because of their thermal stability and low viscosity coefficient and because if breakdown occurs silica forms the residue and there is no tracking.

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## PLASTICS FROM NATURAL POLYMERS (T. N. Parkin, B.Sc., A.R.I.C.)

*British Celanese Limited*

IN the early part of 1948, for the first time in recent years, the supply of plastics based on cellulose acetate, cellulose nitrate, and casein in this country exceeded demand. In the U.S.A. a similar situation arose. The Bureau of Census figures for January to June, 1948, compared with the figures for the corresponding period of 1947<sup>1</sup> show a decrease of about 25% each for both cellulose nitrate and acetate consumption. Comparable figures for the whole of the year are not available nor are there yet any published figures of consumption in this country. Here and in the U.S.A., however, there was a recovery in the last six months, that over here being accelerated by a large increase in demand for sheet for spectacle frames, due to the inception of a free State optical service.

In the injection-moulding field cellulose acetate is having to compete with imported polystyrene, which, in view of the large styrene capacity set free by reduction in synthetic rubber manufacture, is being produced on a very large scale in U.S.A. In this competition polystyrene has the advantage of cheapness, but the superior mechanical properties, especially toughness, of cellulose acetate mouldings are important factors.

With a view to cheapening the manufacture of raw cellulose acetate the investigation of the unit-processes of its manufacture continues, as does the search for cheaper alternatives to cotton linters. Much progress has been made in the conversion of cellulose acetate into plastics and in the working of these plastics, and new or insufficiently exploited uses are being developed.

Owing primarily to shortage of the corresponding acids, there is still no substantial manufacture here of the higher fatty acid esters of cellulose, and cellulose acetate-butyrate is being imported from the U.S.A. Ethyl cellulose is also being imported.

The low cost of cellulose nitrate here gives the nitrate plastics industry an advantage within its restricted field that has been well exploited during 1948, especially in foreign markets.

The casein plastics industry which is now in the happy position of getting its rennet-casein from the Commonwealth rather than from the Argentine, is also competing well with foreign manufacturers. The manufacture of casein buttons here in 1947 was about twice that of 1931, and an even greater production was forecast for 1948.<sup>2</sup>

### Cellulose derivatives suitable for plastics

Continued interest is being shown in alternatives to cotton linters as the basic raw material for cellulose derivatives. No substantial new source of cellulose outside the field of Schieber's wide survey in 1941<sup>3</sup> appears to have been found. Jute, which, according to an Indian report, is a better raw material for cellulose acetate than wood-pulp (98.5%  $\alpha$ -cellulose after a chlorite treatment followed by alkali treatment) seems

unlikely to be available in sufficient quantity or at a low enough price.<sup>4</sup> Jayme has reported favourably on the composition of pulps from poplar wood,<sup>5</sup> and has suggested afforestation with these quick-growing trees in England as well as in Germany.<sup>6</sup> The same author has described a simple method of assessing the reactivity towards acetylation of cellulose pulps and linters,<sup>7</sup> and given further information about the sulphite pulp industry in Germany. The effect of the species of wood, fibre density, and mechanical treatment of pulp (shredding, flaking, etc.) in nitration is discussed by N. O. Schur and D. H. McMurtrie.<sup>8</sup> J. Strachan estimates the annual production of straw in Great Britain at 7 million tons, but his suggestion that most of this should be utilised in cellulose manufacture, the needs of the soil being met by the use of dried sea-weed, seems unlikely to commend itself to agriculturalists.<sup>9</sup>

Karin Wilson has discussed various methods of determining the carboxyl groups in cellulose and devised an improved method.<sup>10</sup>

Various small improvements have been proposed in methods of purifying cotton linters to secure improved clarity and colour in the resulting cellulose derivatives.<sup>11</sup> Improved stability combined with clarity are said to be obtained if the magnesium : calcium ratio in cotton linters is increased by the addition of magnesium salts.<sup>12</sup> It is claimed that delignification can be facilitated by exposure to ultrasonic waves.<sup>13</sup> It has been proposed, in bleaching cellulose by chlorine, to avoid degradation by the presence of a small proportion of ammonia.<sup>14</sup>

In the nitration of cotton linters R. K. Brown and C. B. Purves obtained higher nitrogen contents and lower viscosities when the linters were treated in swollen condition than when collapsed by washing and drying.<sup>15</sup> The mechanism of ammonia stabilisation of cellulose nitrate has been investigated by R. E. Reeves and J. E. Giddens, who attribute the effect to neutralisation of cellulose acid-sulphate or trapped sulphuric acid. Alkylamines were not effective, presumably owing to their large molecule size.<sup>16</sup>

In pretreating cellulose pulp before acetylation it has been claimed that by impregnating the pulp in sheet form with glacial acetic acid and immediately disintegrating, prolonged exposure to the acid, such as is usual, is rendered unnecessary.<sup>17</sup> Details of the I.G. cellulose acetate plant at Dormagen, and its operations (with working drawings), have been published. Acetylation was carried out in methylene chloride. An interesting feature was a continuous washer for the flake provided with means for dealing with caking when wood-pulp was used.<sup>18</sup> A process employing ethylene dichloride or 1 : 3-dichloropropane as diluent, which enables the sulphuric acid catalyst to be reduced to as little as 0.5% of the weight of the cellulose, has been patented.<sup>19</sup> Heuser has acetylated cellulose dissolved in phosphoric acid. At least 50% reduction in degree of polymerisation occurred under the best conditions, which gave partial acetates of variable acetone-solubility. Complete acetylation involved much more degradation.<sup>20</sup> The use of phosphorus oxychloride as catalyst in acetylating cellulose with acetic anhydride in acetic acid has been investigated in an Indian laboratory and stated to give satisfactory triacetate at temperatures up to 120° C.<sup>21</sup> Higher halogen oxides formed *in situ* have also been proposed as acetylation catalysts.<sup>22</sup> By

employing perchloric acid together with sulphuric acid, it is claimed that acetates free from combined sulphur<sup>23</sup> are obtained. P. V. Popov has investigated acetylation by acetyl chloride in a number of inert diluents in the presence and absence of pyridine.<sup>24</sup> P. K. Choudry has presented tabular data on the composition and solubility of cellulose acetate prepared with various proportions of acetic acid and anhydride using sulphuric acid as catalyst.<sup>25</sup> The kinetics of ripening have been investigated by K. Atsuki and I. Kagawa, who found the zinc chloride process to be a reversible reaction, the equilibrium constant of which is decreased by rise in temperature, increased by increase in zinc chloride concentration or addition of calcium chloride, and is unaffected by addition of hydrogen chloride; the sulphuric acid process to be an irreversible reaction catalysed by un-ionised sulphuric acid in proportion to its concentration; and de-polymerisation to be more vigorous the greater the amount of sulphuric acid.<sup>26</sup> Further patents directed to shortening the ripening process by working at elevated temperatures have appeared.<sup>27</sup> Cellulose acetates of improved heat- and flame-resistance have been developed by Hercules Powder Co., and by Koppers Co.

Some doubt has been cast on the validity of the "tosylation" method of Purves for distinguishing primary from secondary hydroxyl groups in cellulose acetate by investigations carried out by Redfern and Boyle,<sup>28</sup> and by Malm and co-workers.<sup>29</sup> It appears that either "tosylation" of the primary groups is a slower process than has been thought, or that the secondary tosyl groups undergo slow iodination.

"Forticel," the cellulose propionate of the Celanese Corporation of America is proving its worth as a basis for mouldings of high impact-strength and water-resistance. "Tenite III," the cellulose acetate-propionate of Tennessee Eastman Corporation, has been withdrawn, apparently because it has no advantages over that Company's improved cellulose acetate-butyrate.<sup>30</sup> In the manufacture of the acetate-butyrate a process has been patented in which the product is freed from esters of low molecular weight by prior precipitation of these by a dialkyl ether.<sup>31</sup> Higher fatty acid esters of cellulose are obtained in a form particularly easy to wash and giving plastics of improved colour, stability, and dielectric strength, if further quantities of the fatty acid diluent are added when esterification is nearly complete.<sup>32</sup> A process for removing residual free fatty acid from higher fatty acid esters of cellulose by extraction has been patented.<sup>33</sup> The manufacture of a cellulose butyrate-crotonate, which gives clear tough mouldings has been patented.<sup>34</sup>

W. P. Untermohlen and E. L. Wallace have investigated the esterification of cellulose diacetate and ethyl cellulose by phthalic anhydride and by tetra-chlorophthalic anhydride, obtaining 70% substitution of free hydroxyl with the unsubstituted, and 39% with the substituted anhydride.<sup>35</sup>

In the etherification of cellulose, some minor improvements have been recorded. A method has been patented in which the alkali-cellulose is made by treating sulphite pulp with hot aqueous alkali which is removed when wetting but not swelling is complete.<sup>36</sup> Patents have appeared for shredding alkali-cellulose made from highly purified wood-pulp after adding a suitable cation-active substance to replace natural

lubricants removed in the purification of the pulp.<sup>37</sup> A process in which etherification of alkali-cellulose, *e.g.*, by ethyl chloride, is carried out in refined kerosene to avoid solution, has been patented.<sup>38</sup>

A Russian investigation has correlated degree of etherification of cotton and ramie fibres by ethyl chloride with solubility and X-ray structure. As substitution increased, crystallinity appeared, but not at as low a degree of substitution as in the case of esterification.<sup>39</sup>

Cellulose ethers of improved heat-stability and clarity have been obtained by solution in non-degrading polar liquids, followed by precipitation.<sup>40</sup>

Various reactions of cellulose derivatives that presumably involve cross-linking may be mentioned here, *viz.*, reaction with an N-alkoxyalkyl polyamide, an alcohol or mercaptan, and formaldehyde<sup>41</sup>; with glyoxal or pyruvic aldehydes<sup>42</sup>; with formaldehyde and a lower alcohol<sup>43</sup>; and with modified urea-formaldehyde resins.<sup>44</sup> Reaction of cellulose esters and ethers with ethylene under high pressure in the presence of a polymerisation catalyst is claimed to give products of superior water-resistance.<sup>45</sup>

### Cellulose derivative plastics: manufacture and use

In the manufacture of cellulose derivative moulding powders, the most important recent advance is plasticisation by spraying with the plasticiser without volatile solvent or diluent. Two patent applications describing the method and apparatus developed for this purpose by the Hungerford Research Corporation have now appeared. The method, which seems likely to be widely adopted, involves tumbling the powdered cellulose derivative, and spraying the plasticiser from jets located near the axis of revolution of the tumbler, so that a fresh surface of the powder is continually presented to the spray and intercepts the spray before it reaches the wall of the tumbler.<sup>46</sup> V. Stannet has described the various methods that have been used in the manufacture of moulding powders.<sup>47</sup> Electronic devices for detecting metallic contaminants in moulding stock, so avoiding damage to moulds and other apparatus, are now in use in the U.S.A.<sup>48</sup>

As heat-stabilisers for cellulose ethers, copper salts have been proposed.<sup>49</sup> Light stabilisers proposed for cellulose derivatives include resorcinol disalicylate<sup>50</sup> and resorcinol monobenzoate.<sup>51</sup> A heat- and flame-resistant cellulose acetate plastic (Lumarith XF) has been developed by Celanese Corporation of America.

In injection moulding, larger and larger machines are coming into use. In this country, there is at least one 40-oz. machine in use. E. F. Bachner has discussed the injection-moulding of large parts.<sup>52</sup> High production rates are obtained in a machine with independent control of spreader temperature.<sup>53</sup> A heating-jacket containing normally solid material, held at its melting point by electrical heaters, is claimed to give more accurate temperature control.<sup>54</sup> An interesting method of making sparking-plug bodies is by injection-moulding ceramic material containing a small proportion of a thermo-plastic binder, *e.g.*, ethyl cellulose, a thermo-setting binder, *e.g.*, shellac, and a plasticiser, hardening the moulding by heat, and then firing.<sup>55</sup>

In comparing the mechanical properties of injection-moulded and compression-moulded articles, the lower strength of the former is attributed by W. Weigel, on the evidence of photo-micrographs, to stratification perpendicular to the direction of injection.<sup>56</sup> A survey of the effect of processing methods on the properties of moulded articles has been given by J. Delmonte.<sup>57</sup> W. O. Bracken has investigated the behaviour of injection mouldings of various materials, including high-acetyl cellulose acetate, cellulose acetate-butyrate, and ethyl cellulose, when exposed to simulated tropical conditions, and the effect upon this behaviour of shape and size of moulding, and process variables such as length of cycle and size of gate.<sup>58</sup>

Extrusion methods of working cellulose derivatives, are becoming increasingly more important. At a meeting of the Plastics Group, S. Booth, H. A. Nancarrow, and J. Jack dealt with design of machinery and dies, temperature control, and the physics of extrusion, including an extension of Ragowski's theory to account for the unexpected fluctuations in extrusion rate sometimes encountered. Various methods of investigation were described, including determination of elastic deformation (which governs swelling at the die), use of the extrusion-rheometer to determine flow properties of material and investigation of flow through dies by extruding cylinders of plastic with stained surfaces.<sup>59</sup> The effect of screw-design in dry extrusion and the critical nature of the temperature of feed, cylinder, screw, and die, for a particular design of screw has been discussed by W. P. Moeller and R. Phillips.<sup>60</sup> Design of apparatus to give extrusion, *inter alia*, of cellulose acetate-butyrate, in tube form to close tolerances has been discussed by G. Jargotoff and C. Joslin.<sup>61</sup>

For heat-sealing cellulose acetate sheet, heating elements coated with polytetrafluorethylene to prevent them sticking to the sheet, are recommended.<sup>62</sup> Progress has been made in developing a technique for high-frequency welding of cellulose acetate sheeting.<sup>63</sup>

An exhibition to encourage the use of cellulose acetate in packaging has been held by British Celanese Ltd. An interesting exhibit was large-diameter thin-walled tubing for packaging made by helical winding of foil with application of an adhesive. W. F. Cullom has discussed the use of plastics in packaging.<sup>64</sup> The gas permeability of acetate foil is an advantage when packaging fresh vegetables and fruit as it allows them to breathe. The combination of water-resistance with high gas-permeability of ethyl cellulose foil makes it particularly suitable for such purposes and for packing meat. The grease-resistance of various packaging materials has been investigated. Cellulose acetate, cellulose nitrate, and ethyl cellulose all afforded high resistance even after ageing at 148° F. and creasing.<sup>65</sup>

The literature shows continued interest in cellulose derivatives as the basis of cellular plastics<sup>66</sup>; as the binding material for laminates (which can be deep-drawn)<sup>67</sup>; and as a basis for adhesives.<sup>68</sup>

The use of cellulose derivatives in paper coating has been discussed<sup>69</sup> and fresh data have been given on hot-melt-coating by ethyl cellulose,<sup>70</sup> and cellulose acetate-butyrate.<sup>71</sup>

K. Tinus has discussed the influence of dipole-moment and self-cohesion on the specific adhesion between two materials, and instanced

suitable interlayers for various pairs of substances.<sup>72</sup> K. Kanamura and K. Yoshino have measured adhesion of cellulose nitrate, cellulose acetate, ethyl cellulose, and benzyl cellulose to copper, iron, nickel, and glass, and derived a formula relating the adhesive power of cellulose nitrate to its degree of polymerisation.<sup>73</sup>

The dielectric properties of cellulose acetate plastics, combined with their mechanical and chemical properties, are leading to their increasing use in the electrical industry.<sup>74</sup>

As a heat-treatment panel a laminate of metallic layers alternating with layers of expanded cellulose acetate has been found very effective.<sup>75</sup>

The optical properties of various plastics, including cellulose derivatives, have been considered,<sup>76</sup> as have the weathering and ageing properties,<sup>77</sup> resistance to water, acids, alkalis, and solvents,<sup>78</sup> general mechanical properties,<sup>79</sup> and the variation of these with temperature.<sup>80</sup> An improved method of measuring scratch-resistance has been described and applied to various cellulose derivative plastics.<sup>81</sup>

### Plasticisers for cellulose derivatives

The mechanism of plasticisation continues to invite investigation and discussion. Although much of the work has been carried out on vinyl polymers, the application of the conclusions to cellulose derivative plastics is often evident. Following his work referred to in a previous Annual Report,<sup>82</sup> A. K. Doolittle has briefly discussed current thermodynamic theory of solvent action on high polymers and has developed his mechanistic theory based on consideration of the opposing solvation and aggregation tendencies of a polymer in contact with a solvent or plasticiser. Threshold concentrations determined by dilution were taken as criteria of solvent ability. Good low-temperature plasticisers showed increase in solvent ability on cooling.<sup>83</sup>

R. F. Boyer and R. S. Spencer have discussed the effect of plasticisers on second-order transition temperatures and allied phenomena (*e.g.*, brittle-point and peak in dielectric loss-factor) and have reviewed the principal theoretical and empirical approaches to a quantitative explanation of the action of plasticisers; derived theoretically a linear relationship between the reciprocal absolute transition-temperature of a polymer-plasticiser composition and the square root of the weight fraction of the polymer, and found this to fit some, but not all, polymer-plasticiser combinations; and successfully correlated brittle-point with the solvent-polymer interaction constant  $\mu$ , for polyvinyl chloride with various plasticisers.<sup>84</sup>

In a paper on "Creep Behaviour of Plasticised Vinylite V.Y.N.W.", W. Aiken, T. Alfrey, A. Janssen, and H. Mark describe a simple technique for investigating the visco-elastic behaviour of plasticised polymer (in film-form) over a time scale range of  $10^{-1}$  to  $10^6$  seconds. By expressing the results as a plot of strain/stress as a function of time, all the plasticisers investigated could be allocated to one of four groups according to the slope and position on the scale of the curve obtained. These curves were correlated with other properties of the plasticiser and with chemical constitution.<sup>85</sup>

At a meeting of the Plastics Group on 13th April, 1948, H. Jones expounded his viscosity theory of plasticiser action. Two kinds of test applied to plasticised polymers to evaluate the plasticiser were considered: tests involving stress and strain; and tests involving energy-dissipation. The property measured in the first kind of test when plotted against temperature, duration of test, plasticiser content or fluidity of plasticiser gave a sigmoid curve. The property measured in the second kind of test when plotted against the same variables gave a curve showing a maximum. Data were provided showing the parallelism for both kinds of test between temperature of test and viscosity of pure plasticiser. It was made clear that anomalous results may be expected when polymer-plasticiser miscibility is incomplete.<sup>86</sup> The same author, with E. Chadwick in a more general survey, has discussed *inter alia*, methods of estimating miscibility and polymer-plasticiser interaction, and the migration of plasticisers from one polymer to another.<sup>87</sup>

The mechanism of plasticiser action has been discussed by P. B. Stickney and L. E. Cheyney, with particular reference to the flexibility of the polymer chain, the polar interaction of groups along the chain, the masking of these groups by plasticiser and the spacing apart of the chains by the plasticiser. In simple cellulose derivatives the rigidity and regular spacing of polar groups are important factors.<sup>88</sup>

P. Clement has given an extensive review of his work on the solvation of cellulose derivatives as investigated by determining the equilibrium concentrations of the cellulose derivative and of the components of a binary solvent mixture, and by infra-red spectroscopy, and has drawn conclusions as to the mechanism of solvation, the various types of bond involved, and the effects of molecule size and dipolar character of polymer and solvent.<sup>89</sup>

In the Goodyear Research Laboratory radioactive phosphorus is being used to trace the migration of plasticisers.<sup>90</sup>

Among new monomeric plasticisers proposed for cellulose derivatives mention may be made of: partially hydrogenated mixed terphenyls, for ethyl cellulose<sup>91</sup>; 3-methyl-4:6-di-*tert.*-butyl cyclohexanol, stated to give low-temperature flexibility combined with light-fastness in cellulose nitrate and ethyl cellulose compositions<sup>92</sup>; ethylene glycol- and diethylene glycol-acetate-benzoates for cellulose acetate<sup>93</sup>; of cyclic acetals derived from 1:2:5:6-tetrahydrobenzaldehyde for cellulose acetate<sup>94</sup>; of morpholides of aromatic and higher aliphatic acids, for cellulose acetate and ethyl cellulose<sup>95</sup>; and of alkoxyl-alkyl, and phenoxy-alkyl esters of lactic acid and other hydroxy carboxylic acids, and acetyl derivatives of such esters, for cellulose acetate.<sup>96</sup>

Polymeric plasticisers are of particular interest on account of their non-volatility and substantial non-mobility. Few have so far been described which are compatible with cellulose acetate, but in this class are polyallyl acetate and other polymeric allyl esters of degree of polymerisation from 6 to 12,<sup>97</sup> and ether-alcohol esters of polymeric lactic acids of degrees of polymerisation from 2 to 4.<sup>98</sup> Ethylene glycol-isopropylene glycol-sebacic acid-maleic acid polyesters have been described as plasticisers for cellulose derivatives, that can be cured.<sup>99</sup>

The performance of various phthalic acid and sebacic acid esters as plasticisers for cellulose acetate-butyrate moulding stock has been investigated by L. W. A. Meyen, of Tennessee Eastman Corp.<sup>99</sup> The use of chlorinated diphenyl, chlorinated naphthalene, and alkyd resin plasticisers for cellulose nitrate has been discussed by C. Salvi.<sup>100</sup> T. Petitpas has surveyed recent work on the gelatinisation of cellulose nitrate, distinguishing agents (*e.g.*, camphor, the ketones, and the acetic esters) which form with the polymers a complex of characteristic crystal structure, from those which do not (*e.g.*, nitric esters). The opening-up effect of methanol facilitating absorption of plasticisers of large molecular weight is referred to.<sup>101</sup> A method for determining camphor in cellulose nitrate films has been described.<sup>102</sup>

A valuable report on the German plasticiser industry, giving preparative details and properties has been published.<sup>103</sup>

### Protein plastics

T. Koch has discussed the production of plastics from rennet- and acid-caseins, soya bean protein and zein with particular reference to the chemistry of hardening by formaldehyde, of sulphur cross-links, and of various after-treatments.<sup>104</sup>

An important investigation carried out by the U.S. Department of Agriculture to find whether casein, suitably pre-treated, could be moulded directly, gave promising results with casein, and especially with carbamido casein (made by reacting casein with potassium cyanate), pre-treated with formaldehyde. Sulphonamide plasticisers increased water resistance whereas most other kinds of plasticiser had the opposite effect.<sup>105</sup> From the same source comes a detailed investigation of the reaction between formaldehyde and casein.<sup>106</sup>

For plasticising proteins, non-hydroscopic amides, aromatic amines, amino-alcohols, and amino-sodium sulphonates have been proposed especially in conjunction with auxiliary plasticisers such as turkey red oil. The preferred agent is formanilide.<sup>107</sup>

The manufacture of buttons from casein sheet and rod in a British factory has been described.<sup>108</sup> In an American survey of the button industry the relative merits of buttons of various materials are considered.<sup>109</sup>

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# RESINS, DRYING OILS, VARNISHES AND PAINTS

BY MEMBERS OF THE OIL AND COLOUR  
CHEMISTS' ASSOCIATION

DRYING OILS, DRIERS, AND VARNISHES (J. H. Greaves,  
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THE continued difficulties of supply of drying oils is reflected by the close attention shown to the properties of hitherto little used oils, such as rubber seed oil; of oils produced by processes not used in this country, such as solvent treated soya bean oil; and of oils from new sources, such as indigenous linseed oil. There has been continued interest in the mechanisms of oxidation and polymerisation.

## Drying oils

In 1948 some valuable experience was obtained of growing in this country, the most important and most widely used drying oil, linseed oil. In spite of abnormal weather conditions being responsible<sup>1</sup> for some poor yields (though the quality of the oil is good) there is optimism in some quarters regarding the future.<sup>2</sup>

Introduction of new varieties and developments in cultivation should make the crop more attractive to the farmer and greater quantities will possibly be grown. Although this production has an important effect on economy, the maximum supply would only be a small fraction of total consumption.

With a view to adding to the well-established drying oils, namely linseed oil, dehydrated castor oil and tung oil, and also stillingia and oiticica oils, there are several others which are undergoing investigation for immediate, or almost immediate, utilisation or cultivation. Although it has been stated<sup>3</sup> that there is a growing realisation of the interchangeability of similar types of drying oils in order to meet conditions imposed by world economic pressure, it is absolutely necessary to make an evaluation of each oil. The wide variety of methods of examination is of interest. For a thorough evaluation<sup>4</sup> there is, of course, an endless number of physical and chemical procedures and simple varnish and paint-making tests. If an oil is completely unknown a straightforward drying test on the oil to which driers have been added gives invaluable information, and yet may not give the *inherent* drying properties. The iodine value has probably been the foremost analytical figure used to provide this information. A quick-drying index,<sup>5</sup> to be distinguished from an index representing general drying properties, has been introduced by T. P. Hilditch. This is calculated directly from the percentage contents of linoleic (*lin*) and linolenic (*len*) acids by the expression  $(lin + len) \times len \div 100$ . An index representing general drying properties has been claimed<sup>6</sup> to be provided by the sum of  $(lin + 2 len)$ . It

has been indicated<sup>7</sup> that this simple expression for an oil is closely related to the iodine value, and further, that the number obtained by subtracting 100 from the iodine value is another suitable index, thus almost completing a circle back to the unadjusted iodine value. Traces of non-glyceride materials, such as rubber in rubber seed oil or the anti-oxidants in crude soya bean oil, may, however, make correlation with actual behaviour by no means direct. Drying indexes based on content of unsaturated fatty acids may be assumed to be useful when applied to triglyceride oils, such as tobacco seed oil, where the constituent acids are probably linoleic, linolenic, oleic, and the other usual acids.

An example of an oil containing appreciable amounts of another acid is stillingia oil, of which large quantities have been used in this country in the past two years. A drying index based on literature figures for the content of linoleic and linolenic acids predicts<sup>8</sup> less satisfactory performance than linseed oil, yet this oil dries faster and to a harder film. A tendency to bloom is removed by polymerisation. At Liverpool University<sup>8</sup> there has been found 5-6% of a constituent acid which is believed to be of low molecular weight and to contain a carbonylic group. If this acid does confer quick-drying hard films, the elucidation of its structure may have an important bearing on knowledge of drying processes and on modification and synthesis of oils.

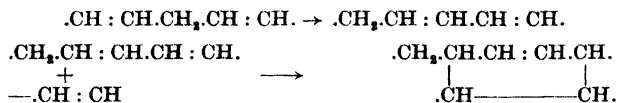
Of the little-known or little used drying oils may be mentioned rubber seed oil,<sup>5,8,9,10</sup> conophor oil,<sup>5,8</sup> and tobacco seed oil. Because it is not available for general use in this country soya bean oil may be included in this classification. This semi-drying-oil is grown and used in considerable quantity in the U.S.A., and has that most important industrial characteristic, non-yellowing. This property, associated with the absence, or almost complete absence, of triply and poly-unsaturated acids is especially important for alkyds. The only drying oil, as distinct from semi-drying oil, of good availability and having such good non-yellowing properties, is dehydrated castor oil, which, however, gives alkyds with a certain tendency to gas-checking. In order to improve the drying properties, quantities of soya oil are subjected to solvent treatments,<sup>11</sup> whereby a fraction is obtained which is more highly unsaturated. Products are obtained having drying characteristics approaching those of linseed oil, and at the same time are non-yellowing. Many different extraction procedures have been described during the last few years, the most widely used probably being counter-current extraction by furfural in a vertical packed tower.<sup>11</sup> Any oil can, of course, be so treated, but soya bean oil has aroused much interest here not only because it has been demonstrated that the process can be successfully worked on the large scale but also because of the tentative suggestion of growing the bean in Africa, and of the outstanding properties just described. Since the various constituent fatty acids are distributed among triglycerides only partial segregation can at best be obtained<sup>12</sup> by solvent treatment of the oil, and more complete separation can theoretically be achieved when there is one fatty acid chain to one molecule of the material being extracted. Two such materials are free fatty acids themselves and monoglycerides.<sup>13</sup>

Of the many other methods of improving or modifying drying properties, a few will be discussed here. Solvents may be used to dissolve the oil, which is then chilled<sup>14</sup> to crystallise out a more saturated fraction separable by a centrifuge. There are some processes depending on ester interchange. It has been demonstrated,<sup>15</sup> using oleic, stearic, and mixed oleic/stearic esters of glycerol, that when mixtures of glycerides are heated at 205°, trans-esterification leads to a stable equilibrium depending only on the amounts of the various acyl radicals present, and that the equilibrium composition can be calculated by the direct application of probability distribution of the acyl groups. If the similar ester interchange among triglycerides containing drying fatty acids can be made to take place at reasonably rates at a sufficiently low temperature, then predominately saturated glycerides will crystallise out. The remaining liquid oil will progressively become more and more unsaturated. It is claimed<sup>16</sup> that by using sodium methoxide as a catalyst an improved drying oil from soya bean oil can be prepared in this way. Another means of removing non-drying fatty acids is based on their greater ease of distillation as compared with the doubly and triply unsaturated acids or their polymers. When a semi-drying oil is heated, for example, with the dimers<sup>17</sup> of unsaturated fatty acids, these tend to an equilibrium with the other acids and under a vacuum non-drying acids are steadily removed. Straightforward heating of an oil with a suitable catalyst, such as anthraquinone, produces<sup>18</sup> a certain amount of conjugation, and is stated to improve drying and to reduce after-tack. So long as tung oil is available for the purpose, and if absence of after-yellowing is not of paramount importance, then the most practicable means of stepping up the performance of both semi-drying and drying-oils is to use this oil for co-polymerisation. A mixture of 3 parts of soya bean oil to 2 parts of tung oil has been found<sup>19</sup> to be equal to or slightly better than linseed oil. Satisfactory drying is still obtained with smaller proportions of tung oil.

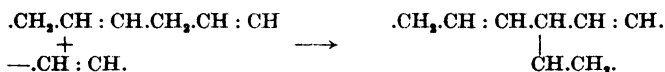
The chemistry of dehydration of castor oil has been examined by C. P. A. Kappelmeier,<sup>20</sup> who observes that during dehydration there is a reduction of saponification value as determined by the usual procedure. As the molecular weight of the triglycerides gets less it would be expected that this value would increase, and in fact it is shown that by using a saponification time of 6 hours increased values are, in fact, obtained. It is also observed that the hydroxyl value of the methyl esters of the fatty acids obtained by complete saponification of dehydrated oil is higher than that of the oil from which they are prepared. To explain these results it is suggested that during dehydration ester interchange occurs between the glyceryl radical and the secondary hydroxyl group of ricinoleic acid to form a difficultly saponifiable ester. Furthermore, it must be assumed that some free hydroxyl groups of the glycerol radicals are destroyed, this also explaining formation of acrolein. It is concluded that hydroxyl value is not a satisfactory measure of the degree of dehydration. Continuous production<sup>21</sup> of dehydrated castor oil has been described in which a thin film of oil runs down inside of a stainless steel tube.

### Polymerisation

The most commonly prevailing suggested course of reaction for the polymerisation of unconjugated drying oils involves isomerisation of two isolated double bonds in a fatty acid chain to the conjugated position, followed by a Diels-Alder addition to a double bond in another chain:



Another suggested mechanism is the union of two acid chains by "hydrogen separation":



A paper by E. Sunderland,<sup>22</sup> in which this second reaction received some support initiated an interesting series of comments and discussion. T. F. Bradley<sup>23</sup> strongly supports the first mechanism and compares this with the known course of reaction of some simple hydrocarbons analogous in structure to drying oils, for example, butadiene and 1:4-pentadiene. I. M. Bernstein<sup>24</sup> emphasises the importance of molecular weight determinations and finds in a linseed stand oil polymers as large as heptamers. The method of examining this stand oil is fractionation by extraction with a series of monohydric alcohols of increasing chain length. D. A. Sutton<sup>25</sup> points out it has not yet been proved that the linkage between the fatty acids chains in tung stand oil and in linseed stand oil are the same and that the second mechanism has a simple analogue. This worker confirms that there is material of high molecular weight,<sup>26</sup> much above 2500, present in highly viscous fractions from linseed stand oil. H. S. Lilley<sup>27</sup> discusses the significance of the two molecular weight averages, the number average and the weight average. The importance of work on polyfunctionality of polymerising systems is emphasised, especially with regards to calculation of gel point<sup>28</sup> and molecular weight distribution.

### Drying and driers

The drying of linseed oil in the presence of cobalt driers with varying oxygen concentration and film thickness has been investigated.<sup>29</sup> As the partial pressure of oxygen (mixed with carbon dioxide) decreases, so does the amount taken up by the film when drying, the minimum being 7-8%. The lower the oxygen concentration, the more rapid, in relation to oxygen uptake, is the fall in iodine value and the increase in refractive index. Thicker films absorb less oxygen at the touch-dry stage. Volatile oxidation products from the drying linseed oil films appear sometimes to accelerate and sometimes to retard the drying rate of another film. It is deduced that at low oxygen concentration the drying mechanism is abnormal. In the presence of only one of the driers lead, manganese, and cobalt, the colour of the incident light<sup>30</sup> has been found to have a marked effect on the rate of the drying of linseed oil films, for example, violet light accelerates and red light decelerates. The colour of the light

makes no difference when the three drier metals are present together. Following experiments on the autoxidation of linseed oil in the presence of chromium, iron, cobalt, manganese, and nickel soaps, it has been suggested<sup>31</sup> that a measure of the power of a metal to act as a drier is provided by the product of two factors. These are (i) the ease of reducibility from the trivalent state, and (ii) the proportion of the metal in the trivalent state present in the oil.

### Analysis

A rapid method<sup>32</sup> for the colorimetric estimation of cobalt depends on the intensity of the colour of the blue thiocyanate in non-aqueous medium. When iron is present the red iron thiocyanate colour can be removed by the use of ammonium fluoride.

Ultra-violet spectrophotometry is now a standard invaluable procedure for investigation of drying oil structures, but due care has to be exercised in the interpretation of results.

The method<sup>33</sup> of determining linolenic acid by isomerising with alkali and then estimating the conjugated form by the ultra-violet spectrophotometer has been critically examined. Experiments gave an absorption at 268 m $\mu$ . when linolenic acid could not be confirmed by the formation of hexabromostearic acid. Apparently there is liable to be some extraneous adsorption, and it is recommended that small amounts of linolenic determined spectrophotometrically should be ignored unless otherwise confirmed.

So as to investigate<sup>34</sup> oil films during and after drying the dried films are quickly dissolved in alcoholic potash. Formation of conjugated dienes and trienes is found to occur in the early life of a film, followed by a slow decrease after the gelation stage.

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## NATURAL AND SYNTHETIC RESINS (R. S. Robinson, F.R.I.C., A.R.T.C.S., A.P.I.)

*Messrs. Styrene Co-polymers Ltd.*

THERE appears to have been an increase in the research and development on synthetic resins during the past 12 months, presumably due to the rebirth of competition in the industry. This is indicated by the very large number of patent applications which have been filed. Of interest in experimental work relating to the reactions involved in resin formation is that of M. N. Fineman and I. E. Puddington<sup>1</sup> on the electrical resistance changes which take place during the curing of poly-condensation products. By measurement of these changes they have determined the extent to which cross-linking occurs with various resins and under different conditions. Estimation of the oxygen absorption of films of numerous resins has been carried out by J. W. Westwater,<sup>2</sup> who concludes that the orientation of the film plays an important part in this phenomenon. Drying oils are still amongst the most important raw materials used in the preparation of synthetic resins for the surface coating and allied industries, and C. P. A. Kappelmeier has discussed<sup>3</sup> the chemistry of the reactions involved in the many different ways in which they find employment. Methods for the determination of molecular weight distribution are always of interest to the resin chemist and in this respect a simplified small-scale fractionation method has been described by R. S. Spencer.<sup>4</sup> After describing a modified method for the determination of the "isodiene value" of resins, Durr and Wendling indicate<sup>5</sup> how its application can be used to control the course of resinification. Owing to the shortage and high price of linseed oil, the engineering industry has

taken an interest in synthetic resins with regard to their employment as core-binders. It has been found that phenolic types are suitable for steel castings, whereas urea resins are more satisfactory for use with iron, brass, and aluminium.<sup>6</sup>

### Natural resins

A method of increasing the production of oleo-resins and gums by coniferous trees has been claimed which comprises injecting an isolated spore of a fungus.<sup>7</sup> G. C. Harris and T. F. Sanderson<sup>8</sup> report the presence in rosin of a new acid which they call "neo-abietic acid," and which they isolated by employing a fractionation method based on the crystallisation of its amine salts. That anhydrides are formed during the thermal processing of rosin is believed by G. A. Vasil'ev to have been confirmed.<sup>9</sup> An account has been given<sup>10</sup> of the commercial production of a fossil resin, similar to kauri, from the Utah coal deposits. An analysis of Dammar has indicated that 50% of this resin consists of alcohols of the triterpene group.<sup>11</sup>

### Alkyd resins

Recent developments in the production of alkyd resins have been reviewed by F. C. Ruzicka,<sup>12</sup> who shows how maleic anhydride is steadily replacing phthalic anhydride. The use of the addition product of maleic anhydride and cyclopentadiene as the polybasic acid reactant has been known for some time, but S. R. W. Martin<sup>13</sup> now claims that this product can be prepared *in situ* from its components during the preparation of oil-modified alkyd resins. A new series of resinous polybasic acids for use in alkyd resin manufacture is described by E. A. Bevan and R. S. Robinson.<sup>14</sup> These acids are prepared by the thermal reactions of certain aldehydes and ketones with maleic anhydride, and the chemical character of these reactions is such that modification with phenols, styrene, etc., is a relatively simple procedure. An interesting preparation of a phenol-modified alkyd has been described by L. Coes<sup>15</sup> in which penta-erythritol diformal is reacted with a mixture of a phenol and a polybasic acid. The formal breaks down to give the alcohol and formaldehyde which then react with the acid and phenol respectively. The styrene modification of alkyd resins is receiving a great deal of attention as is indicated by the considerable number of patents which are being filed relating to this subject, and at least one such product suitable for use in the surface coating industry is already in production on a commercial scale in this country. A styrene-alkyd co-polymer for use in the low pressure process for the manufacture of laminates has also been described.<sup>16</sup> The effect on film-gloss resulting from the use of different solvents in oil-modified alkyd finishes has been reported by K. van Lerberghe.<sup>17</sup>

### Phenolic resins

The question of the structure of phenol-formaldehyde resins is still receiving attention. H. S. Lilley<sup>18</sup> has given consideration to this using mono-reactive phenol alcohols as models, and C. A. Redfarn has reported results of work<sup>19</sup> which suggests that the phenolic hydroxyl group enters into the cross-linking. It has been confirmed that in acid catalysis all

reactions lead to the formation of methylene bridges.<sup>20</sup> The after-yellowing tendencies of phenol-formaldehyde resins and varnishes made therefrom, and which has been attributed to the presence of unconverted phenol, have been avoided by reacting the products with  $C_9$ - $C_{18}$  fatty acids.<sup>21,22</sup> The production of internally plasticised phenolic resins has been described by T. J. Herman.<sup>23</sup> The phenols are first converted into poly-phenols by reaction with poly-olefins before being treated with formaldehyde.

### Amino-formaldehyde resins

It was formerly assumed that during the curing of urea-formaldehyde resins, linear polymers result. It has now been found by Marvel and his colleagues that cyclic trimers are produced.<sup>24</sup> Resins which are compatible with alkyds without treatment with an alcohol have been prepared by allowing formaldehyde to react with a 1-arylguanazole under alkaline conditions.<sup>25</sup> C. S. Marvel<sup>26</sup> claims the preparation of amino-resins which when air-dry give hard, water-resistant films, such resins being made from glycinamide and formalin. In a British patent,<sup>27</sup> American Cyanamid Co. claim the use of melamine-formaldehyde modified styrene-alkyd co-polymers for craze-resistant wood surfacings. The employment of alkyl ammonium phosphates as "delayed action" curing catalysts for amino-resins is described by L. A. Gruenwald.<sup>28</sup>

### Vinyl co-polymers

Of these, those derived from styrene are receiving the greatest attention in the field of surface-coatings. Styrene-drying oil co-polymers are by now fairly well known and as already stated at least one styrene modified alkyd resin is now on the British market. A description<sup>29</sup> has been given of a plant for the co-polymerisation of styrene and drying oils. Alkyl-aryl-monoamines of secondary or tertiary character have been claimed as powerful activators for use with peroxide catalysts in oil-phase polymerisations.<sup>30</sup> The equilibrium between polymerisation and degradation in styrene reactions has been investigated<sup>31</sup> under varying conditions of temperature, concentration, and catalysis. The superiority of spectrophotometric methods over solubility methods for the estimation of monomeric styrene in polymers has been shown by McGovern, Grim, and Teach.<sup>32</sup> Styrene has been co-polymerised with cashew nutshell liquid and these products can be reacted with aldehydes.<sup>33</sup>

Silicon-containing ethenoid resins have been described by I.C.I. Ltd.<sup>34</sup> in the preparation of which methyl methacrylate or styrene is co-polymerised with an unsaturated ester of silicic acid. The same company also claims the production of a new series of fluorine-containing polymers suitable for the use in surface-coatings.<sup>35</sup> These are made by the reaction of acetylene with fluorinated carboxylic acids and they are stated to produce tough, colourless films of good flexibility. The preparation of vinyl esters of fatty oil acids has also been receiving some attention. One patent<sup>36</sup> describes the formation of these by a process of ester-interchange between the fatty acids and vinyl acetate using a mercuric acetate/sulphuric acid catalyst, whereas in another<sup>37</sup> the fatty acids are treated with acetylene under elevated pressure and temperature employing

zinc oxide as the catalyst. The co-polymerisation of such vinyl esters of fatty acids with vinyl acetate to give useful resins has been reported by Swern, Billen, and Knight.<sup>38</sup>

### Polyamides and urethanes

The poor solubilities of polyamides of the "Nylon" type in common organic solvents has been a serious drawback to the employment of these resins in the manufacture of coatings. A considerable increase in these solubilities and improvements in flexibility, however, has been claimed<sup>39</sup> by a process involving the reaction of linear polyamides with formaldehyde under aqueous alkaline conditions. Du Pont de Nemours<sup>40</sup> treat nylon with formaldehyde under acid conditions in the presence of an alcohol. Di-isocyanate modified polymers have also been treated with formaldehyde<sup>41</sup> to increase flexibility and resilience. A. G. Hovey has described the manufacture of polyamide resins from dimerised soya bean oil fatty acids.<sup>42</sup>

### Silicon types

The number of patents taken out covering modifications of the processes of manufacturing silicone resins is still extremely large, probably exceeding that of patents relating to any other type of resin. F. Chapman<sup>43</sup> has made a comprehensive review of the uses of these resins in paints, in which he discusses their compatibilities with other resins. Amongst the recent patents is one<sup>44</sup> describing the employment of boric anhydride as an agent for furthering the polymerisation of silicones. The co-polymerisation of immiscible organo-siloxanes has been carried out by a thermal reaction in which a current of air is passed through the system until it has assumed homogeneity.<sup>45</sup> A resin which it is claimed can be used for the preparation of highly water repellent surfaces, and which is prepared by heat polymerisation of tertiary-alkoxy-aminosilanes has been reported by C. S. Miner and L. A. Bryan.<sup>46</sup> For the production of silicone resins, the functionality of the monomer is of great importance on account of its influence on the degree of cross-linking and chain-termination, and methods for the estimation of this functionality have been given by G. F. Rodel.<sup>47</sup>

The introduction of silicones in the surface-coating industry has stimulated interest in other silicon-containing resins, particularly the alkyl polysilicates which are comparatively cheap and readily prepared. The uses of these esters in paints have been summarised by H. G. Emblem and J. N. Read.<sup>48</sup>

### Miscellaneous synthetic resins

In America the possibility of utilising lactic acid as the basic raw material in the manufacture of useful resins is receiving some consideration. The preparation of drying-oil-modified poly-lactic resins is claimed in a patent taken out by the U.S. Secretary of Agriculture,<sup>49</sup> and the uses of such resins in the surface coating industry is also described by P. D. Watson.<sup>50</sup> A synthetic resin possessing air-drying properties has been made by treating polymethylene glycols with unsaturated aldehydes.<sup>51</sup>

The Monsanto Chemical Co. claim<sup>52</sup> that a varnish resin can be made by heating together styrene oxide and a phenol. It is stated that varnishes made from these resins with drying oils have very good weather resistance. A series of synthetic resins having many chemical similarities to polypeptides is described by E. A. Bevan and R. S. Robinson.<sup>53</sup> These resins are obtained as a result of the reactions between maleic anhydride or similar unsaturated acids and ammonia or urea. Resinous products have been obtained from drying oils by a rapid process involving the use of a catalyst comprising boric acid and oxalic acid.<sup>54</sup>

Two interesting uses of inorganic materials in the preparation of resins are the polymerisation of organic titanates, principally the butyl ester<sup>55</sup> and the reactions of organic phosphorus halides with dihydric phenols.<sup>56</sup> It is claimed that lacquers made from these latter resins can be used for the production of surfaces having a high resistance to acids.

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## PAINTS AND PIGMENTS (L. J. Brooks, A.R.I.C.)

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THERE is seldom in any one year any advance of great novelty, but there are, as in this year under review, the completion and unfolding of the many activities of recent years. For example, the new non-chalking rutile titanium pigments will shortly take their place in British paint formulations as they have already done in the less sorely-pressed American industry; and the styrene oil co-polymers and styrenated alkyds are further additions to the paint formulator's choice of suitable ingredients.

The rapidly increasing tendency for specialisation of paints to meet particular conditions of performance, or permit some new technique in application continues to develop, for example: paints required for heat resistance, fouling, and corrosion, tropical conditions, mildew, cement surfaces, especially severe conditions of exposure, abrasion, or chemical attack, flame-sprayed plastics, and the modern technique of hammered and polychromatic finishes.

In the literature of pigments there are few items of interest to report; but there are several comments on the relatively newer materials of silicate white lead, and lead titanate. The desirability, on general principles, of incorporating a proportion of reactive soap-forming pigments, such as white lead, basic white lead sulphate, and zinc oxide is prevalent American practice; and is advocated, for example, by F. J. Williams and A. R. Pitrot,<sup>1</sup> who further consider the extension of this principle to the surface coating of an inert pigment by an active one, *viz.* the surface treatment of very fine silica by solid-phase reaction with lead oxide in the presence of lead sulphate to form lead silicates. It is claimed that this method, developed from first principles, provides an

economical and scientifically efficient means of utilising the essential contribution of the reactive component to the life of the film. The resulting pigment complex has a very low specific gravity and high bulking value, and possesses the desirable soap-forming characteristics of a lead pigment with its concomitant increase in durability. E. P. Peterson<sup>2</sup> confirms, from numerous exposure tests, the complete interchangeability of this pigment with normally reactive white pigments in multiple pigment formulations, and shows that the co-reaction with lead sulphate confers light stability absent from lead silicate alone. It is conceded, however, that the product is deficient in opacity and this must be remedied by incorporation with other pigments of stronger hiding power.

Considerable claims are made by J. Rinse<sup>3</sup> for another lead complex, *viz.*, lead titanate. From extensive architectural and marine experience in Holland its durability is considered to be superior to any other white pigment, and is of particular value in an alkyd medium. The general characteristics are described, and the results of hiding power, water absorption, and gloss retention determinations demonstrate its attractiveness. Its mould resistance is, however, limited, and the addition of a fungicide is advised. Lead titanate is not suitable in simple linseed oil media and requires a reinforced vehicle (preferably with tung oil) or a long oil alkyd. It does not settle or liver; and although compatible with other pigments the dilution effect does not improve its properties. It is used to greatest advantage in top-coats as it cannot replace red lead or zinc chromate in primers of anti-corrosive properties, and, finally, its use with phthalocyanine blue in blue tints is said to be unequalled. Favourable comparison of lead titanate with the best non-chalking titanium pigments is reported by W. G. Vannoy and J. F. Brocker<sup>4</sup> in a review of house paint progress. They also add that it has, however, the disadvantage of requiring very high pigmentation.

There has also been rather more than normal interest expressed in the more familiar lead pigments. The crystallography of lead chromes has, for example, been made a subject of careful study by H. F. Clay and Y. Watson,<sup>5</sup> and a clearer appreciation of structural differences and their corresponding effects on pigmentary properties has been made available. From experimental work in which the internal and external structures of various lead chromes were examined by X-ray analysis and electron micrographs respectively, it would appear that certain misapprehensions relating to structure and colour properties have been resolved; it is shown, for example, that the orthorhombic form is not necessarily paler than the monoclinic, because in the case of chromes prepared from litharge-acid mixtures the structural change from rhombic to monoclinic is often accompanied by a change from a redder to a paler colour. It is suggested from this work that contrary to prevalent opinion the shade change produced when a proportion of lead sulphate is incorporated is not due to a structural difference, although lattice deformation undoubtedly makes contribution to the change. Electron-micrographs are presented to show the different forms of acetate, nitrate, and chloride chromes, and it is shown that the rapidity of the polymorphic change depends on the anion used.

A similar study of the structure of lemon chromes is presented by

A. Karaus and M. T. Tabellini.<sup>6</sup> It is considered that the development of dichroism is due to the aggregation of monoclinic crystals. It is claimed that stability during filtration, washing, and drying is achieved by co-precipitation with aluminium hydroxide; and it is shown generally that increase in hiding power and tinting strength is favoured by small crystal size.

This general interest in the lead family of pigments is marked, and includes, besides, interest in the familiar lead chromes and red lead, such relatively new arrivals as lead titanate, lead silicate (*loc. cit.*), lead cyanamide, and lead salicylate. The latter is listed in a useful review<sup>7</sup> of new raw materials, and its preparation as a pigment described in a patent<sup>8</sup> in which salicylic acid is added to a slurry of litharge.

The protective value of metallic coatings in various forms is a subject of considerable activity. These include aluminium, zinc flake, stainless steel, lead-coated pigments, and tin undercoats. The properties of aluminium flake pigments are well-known and its improvement and extensions have been well substantiated. Certain distinct developments in aluminium paste pigments are claimed by R. I. Wray<sup>9</sup>; improved manufacturing procedure, for example, has increased the aluminium content of the standard paste from 65 to 74% and the product exhibits greater brilliancy and uniformity. A similar improvement in the extra-fine lining type is reported giving good levelling properties and a truer "chrome-like" finish. A third interesting type is described as a hydro paste *i.e.*, one miscible with water; it is, however, non-leafing and limited in application.

Particular interest is expressed in the non-leafing forms which in suitable media have made possible the attractive technique of hammered and polychromatic finishes, and the development of non-leafing aluminium pastes are described. G. W. Wendon,<sup>10</sup> who has examined the relations governing the settling of the Al powders, shows, for example, that the ratio of diameter and thickness of flake is of greater significance than thickness alone, although generally speaking a high sedimentation rate and small sediment volume are functions of increasing average thickness of the flakes. A ball-milled powder is generally more voluminous than a stamped powder and has a correspondingly lower sedimentation velocity and higher sediment volume.

Anti-corrosive properties are claimed by H. Wagner<sup>11</sup> for aluminium and Al/Si alloy pigments coated with lead, by electro-chemical depositions. The use of metallic zinc powder as a constituent of anti-corrosive paints is well-known, but the development of a bright zinc flake is somewhat novel.<sup>12</sup> It is said to combine the familiar electrolytic advantages of the powder in anti-corrosive coatings on steel with a bright metallic lustre. In addition, it is proposed as an excellent constituent of heat-resistant finishes required for exhausts, stacks, funnels, and heat exchangers, preferably in conjunction with asbestine in an alkyd medium. At the high temperature to which it may be exposed, the zinc is claimed to remain intact by alloying with the steel structure after the combustion of the organic binder.

Some of the advantages of stainless steel are attributed to its use as a finely divided powder in normal paint media and in silicone resin

media; in common with aluminium and tin, it is said<sup>13</sup> to give films capable of resisting exceptional heat, and temperatures up to 538° C. have been withstood. And finally it has been suggested that the familiar conception of tin-plating in the canning industry is capable of wider extension for general use as a protective coating under anti-corrosive paints. S. G. Britton<sup>14</sup> describes work by the Tin Research Institute which indicates the value of such coatings for paints used in sea-water and in industrial atmosphere. Although the matter is still a subject of co-operative research between the Tin Research Institute and the Zinc Development Association it would appear that tin-coatings are generally preferable to those of zinc, for example, under ships' compositions. Despite the development of rust at "holidays" and scratches, it is considered, from the mechanism advanced, that the anodic alkali formed is limited in its action to precipitating the iron salts in the sphere of reaction and does not proceed to saponify and soften the paint film as is said to be the case where zinc is used. The thin coating of tin may be applied in several ways of which electro-chemical deposition is the most effective when otherwise convenient, and has the further advantage of providing a matt surface more suitable for painting. It may also be applied by a "wiping" technique in which powdered tin or solder is melted on to the steel surface by a blow-lamp and spread by wiping with a cloth. In the ensuing discussion the comparative merits of tin, aluminium, and zinc were discussed, and it was suggested that tin might prove very promising as an undercoat for high-duty under-water paints, *e.g.*, in the vicinity of ships' propellers.

One of the unavoidable factors in the complete assessment of paint performance is time, and it is one which no system of accelerated test, however ingenious and comprehensive, has succeeded in eliminating completely. It is therefore of interest to note the results of extensive outdoor exposure tests<sup>15</sup> which, particularly in America, have been in operation for several years. The general improvement in decorative paints due to the evolution in use of major-white pigments from: white lead to zinc oxide-lithopone-antimony oxide-titanium oxide, and, finally, to the newer types of non-chalking rutile is generally confirmed<sup>16</sup>; but J. Macguffie,<sup>17</sup> who describes the characteristics of various "Titanox" titanium pigments, considers that correct formulation of white exterior house paints still requires a careful balancing of otherwise competing properties. Outstanding as these new non-chalking titanium pigments are in opacity, pigmentary properties, and the maintenance of film integrity, there is, nevertheless, a tendency to accept them with reserve in white finishing paints as they tend to suffer loss of colour, dirt collection, and mildew.<sup>18</sup> Their desirable properties are considered to appear to best advantage in under-coats, and their non-chalking character makes them eminently suitable for tinted paints. Otherwise the free chalking, and hence self-cleansing properties of the anatase pigment is said to be much preferred in the U.S.A. for white, especially exterior, white house finishes. Opinion on this point varies, Canadian and British users are less inclined to accept free chalking as a desirable quality. A typical white house-paint formulation which has given excellent results in exposure tests over 4½ years is given as: 15/50/35 titanium oxide/35% leaded zinc

oxide/magnesium silicate ; the first is a free chalking titanium, the second controls chalking and inhibits mildew, and, thirdly, magnesium silicate is a generally preferred extender.

The U.S.A. Navy Department appear to be particularly active in promoting the development of all kinds of ships' paints, in particular, those which exercise some special function of protection, such as : anti-corrosive, anti-fouling, fire-retardance, and wood preservation ; as some of the following reports may show.

The general character of orthodox anti-fouling paints renders them unsuitable for flying-boats ; a special composition was therefore developed<sup>19</sup> containing 8% calomel dispersed in chlorinated rubber stabilised by phenoxy propylene oxide and including a proportion of copper resinate which although ineffective as a poison, was found to be indispensable in maintaining suspension and package stability. The composition is said to provide fouling resistance up to 8 months and has the required attribute of a thin, hard, smooth surface ; in addition, it permits a wider range of colour variation than is possible with conventional anti-fouling based on cuprous oxide.

In a further contribution to the valuable series of communications on anti-fouling research from the Woods Hole Oceanographic Institution, B. H. Ketchum<sup>20</sup> gives details of an accelerated leaching rate method which is claimed to provide tentative evaluation of anti-fouling paints in advance of lengthy exposure tests and permit the speedy elimination of unpromising formulations. The method is based on the use of glycine as the leaching solution.

The determination of the electrolytic resistance of under-water anti-corrosive is said to provide another accelerated test of considerable merit<sup>21</sup> ; and a complete correspondence is claimed between the results of 300 systems based on such tests and the more lengthy laboratory weathering tests and service experience. The method is based on the barrier theory that the ionic mobility within a coating is related to the ease of passage of corrosive constituents through the film to the metal substrate. The determination is made by the standard technique for measuring internal battery resistance with a special reference electrode of Hg/HgCl/sea-water. The systems studied included red lead/vinyl resin, zinc tetra-oxychromate polyvinyl/butyl primer with cuprous oxide anti-fouling, and the U.S.A. Navy alkyd topside paint. The advantage of pre-treating the steel with a phosphoric acid-zinc chromate-vinyl resin conversion coating before application of the primer was markedly confirmed. Pigmentation with titanium gave very poor results. The importance of film thickness is confirmed by studies of the rosin-wax hot plastic type of naval protective ; which at 2 mls. thickness failed in two weeks, 4 mls. three months, 6 mls. nine months, and no failure was observed at 8 mls. thickness after 15 months ; these values were exactly confirmed by the laboratory resistance determinations. It was concluded that good protection was obtained at resistance greater than  $\log. R = 8$  and poor protection at resistance less than  $\log. R = 6$ .

The importance of using an effective wood preservative such as : copper naphthenate, chlorinated phenol or phenyl mercury oleate as a separate treatment but in conjunction with a good orthodox wood primer

was shown<sup>22</sup> to give very good results in tests on the numerous small wooden craft used by the Allied Navies, and were a decided improvement on similar preservatives based on zinc chloride or creosote. Any attempt to combine primer and preservative in one composition proved useless as a wood-preservative and deleterious to the final finishing paint.

The experimental and practical difficulties of providing a comparative test of fire retardant paints may be appreciated, hence a thermo-electric method has been developed<sup>23</sup> which depends upon the heat generated in short circuiting a current across the specimen. Tests of over 100 panels show the method to be very consistent and it confirms the value of antimony oxide and/or chlorinated paraffin at present widely used in U.S.A. Navy fire-resistant paints. Antimony oxide alone in high P/V ratio in an alkyd medium may be used provided a flat finish only is required, but in gloss finishes a minimum of chlorinated binder is essential. The use of silicone resins as media for fire-resistant paints is now well advanced, but their high cost renders them of limited application, and it is therefore of interest to note the recent development of titanium esters,<sup>4</sup> in particular, butyl titanate, which when formulated with an alkyd resin (*viz.*, Beckosol 1323) and a strongly leaping aluminium powder is claimed to provide flue and stack paints of exceptional heat-resistant character, and continuous exposure to temperatures up to 500° C. are reported. The "can" stability is also said to be very good, and in this respect much superior to its better known analogue ethyl silicate. The polymerisation of butyl titanate, and the preparation of titanium modified oils and phenolic resins offer very interesting possibilities in improving the durability of conventional paints.

The interest of American official departments in paint research is paralleled only by the considerable activity of the Marine Corrosion Committee and this report would be incomplete without reference to at least some of the numerous publications of the Iron and Steel Institute, which have appeared in the period under review. J. C. Hudson and T. A. Banfield<sup>25</sup> describe the results of a considerable exposure scheme involving the protection of steel by non-metallic paint where the steel has been merely weathered and wire-brushed. Hot plastic type paints, rubber-wax sheathing, and cement-asbestos coatings showed good results over five years; and vitreous enamels were in particularly good condition, even after two years in the sea.

H. Barnes<sup>26</sup> makes further interesting contributions to a study of anti-fouling compositions, and in an investigation of the formation of rosin soaps in such compositions suggests a mechanism for the familiar conception of anti-fouling action by erosion or "exfoliation" in which the acidic rosin acids of the binder are slowly removed by the saponifying action of the slightly alkaline sea-water, thus exposing and renewing contact between the toxic solute and the solvent sea-water. It is shown experimentally that the reaction between the cuprous oxide and rosin *in situ* in the paint during milling and storage may seriously reduce the availability of saponifiable rosin and hence adversely affect the correct performance of this type of paint, which depends upon a degree of controlled degradation in order to maintain its optimum leaching rate.

The development and study of paints prepared from zinc oxychloride

cements is described by J. E. O. Mayne and R. S. Thornhill,<sup>27</sup> who investigated the mechanism of setting and examined the reaction of zinc dust with numerous metallic chlorides, of which  $MgCl_2$  and  $CaCl_2$  were generally the most satisfactory. Consideration of the potentials of immersed steel specimens show that unchanged zinc can maintain its protective cathodic rôle provided the contact resistance is less than the electrolytic resistance. Cement mixtures containing arsenic had considerable protective value due to the absorption of the arsenic on the steel. The marine exposure of such cementiferous schemes have been described by K. A. Pyefinch,<sup>28</sup> and indicate considerable promise provided that the coating is followed by both an oleo-resinous protective coating and then a normal anti-fouling finishing coat.

Certain pertinent reflections on the complex character of anti-fouling research have been made by H. W. Keenan<sup>29</sup> in a brief review. Attention is directed to the desirability of integrating its several aspects which must necessarily include, for example, not only the valuable biological principles but the essential practical information provided by Docking Reports. These reports, incidentally, reveal the very real difficulties which the industry had encountered during the past 30 years. The address includes a brief description of a leaching rate method devised by H. W. Keenan and L. J. Brooks and a complementary investigation of film permeabilities by H. W. Keenan and C. F. Drake.

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**CELLULOSE ESTER AND ETHER-LACQUERS (H. L. Howard, B.Sc., A.R.C.S., D.I.C., M.I.Chem.E., F.R.I.C.)**

EVALUATION of resins for use in nitrocellulose lacquers has in general been carried out in a very haphazard manner in the past, and the Birmingham P.V.L. Club have proposed<sup>1</sup> a method by which such resins may be evaluated in a more fundamental and comprehensive manner. Clear lacquers containing 15% nitrocellulose and having nitrocellulose-resin ratios of 2.0, 1.0, and 0.5 are first prepared and reduced to equal viscosity by means of standard thinner. The amount of plasticiser to be used is such that the lacquer will pass a prescribed print resistance test and the minimum amount which will pass a bend test using an  $\frac{1}{8}$ -in. mandrel is selected. All subsequent tests are carried out on such compositions, which are tested as clear, white, and black, pigmented finishes under comparable conditions, and from these tests an assessment of the resin is made. The Los Angeles Production Club<sup>2</sup> observe that soft resins are less retentive of solvent than the fast-hardening maleic resins, nitrocellulose itself being the most retentive of all. Hard resins, therefore, promote rapid hardening of films, in spite of the retention of solvent, by virtue of their intrinsic properties. A survey of the finishing systems used on aircraft and of the specifications covering their use is given by R. J. Ledwith.<sup>3</sup> Electrostatic equipment for spray coating and de-tearing of dip-coated articles is described.<sup>4</sup>

*Plasticisers*

The fundamental factors involved in the evaluation of plasticiser efficiency are being investigated from several angles. According to the "viscosity theory of plasticiser action" the viscosity of the plasticiser is of paramount importance in defining the physical and mechanical properties of plasticised polymer complexes. It has now become apparent that the original concepts of this theory are applicable to polymers generally and to any temperature range, whether above or below 0°. H. Jones<sup>5</sup> stresses the inter-dependence of the effects of temperature, time of test, and concentration of plasticiser. At low temperatures immiscibility may be induced, but owing to high viscosity, separation of two phases may occur very slowly. Under such conditions internal resolution may occur but may not be apparent, and this may account for the "cheesy" condition often encountered in practice. It is possible that such macroscopic dispersion of the plasticiser may have a more pronounced softening action than normal, and there is some evidence that this softening action may become apparent before conditions of immiscibility are actually reached. It is suggested that it may be possible to take advantage of this abnormal softening in certain circumstances. In any case such anomalous cases should be further investigated with a view to elucidating further the mechanism of plasticiser-polymer interaction. G. J. Dienes and F. D. Dexter<sup>7</sup> have investigated the logarithm stiffness-temperature curves of various plastics, and find the effect of the plasticiser is to shift the curve laterally along the temperature axis in the direction of lower temperature as the amount of plasticiser

is increased. The slope of the curve is an index of temperature sensitivity of the plasticiser and is approximately constant over the 20–45% range. Its magnitude is characteristic for any given resin–plasticiser system. L. W. A. Meyer and W. M. Gearhart<sup>8</sup> have examined the efficiency of phthalic and sebacic esters as plasticisers for acetate–butyrate cellulose esters. Sebacic esters exhibit less solvent power than phthalic, and 2-ethyl hexyl sebacate is such a poor solvent that even with 50% acetone it will not dissolve the cellulose ester and at low temperatures its use results in cheesy structure. Results are in general agreement with the “viscosity theory,” but some anomalous results are noted. A group of patents by British Celanese Ltd. claim the use of derivatives of substituted butanols,<sup>9</sup> butanones,<sup>10</sup> hexahydrobenzyl alcohols,<sup>11</sup> and benzadol<sup>12</sup> as plasticisers. Esters of naphthenic acids show no discoloration with ultra-violet light,<sup>13</sup> esters of tetrachlorophthalic acid<sup>14</sup> are proposed as non-flam plasticisers for nitrocellulose and toluene sulphonamide<sup>15</sup> is claimed to improve gloss, clarity, and adhesion of nitrocellulose. The use of derivatives of cyclohexyl carbinol is also covered.<sup>16</sup>

### Testing

H. Green and T. P. Lamattina<sup>17</sup> describe an apparatus for the determination of adherence of organic coatings to metal surfaces. A loaded broad knife edge, connected to a balanced lever, rests on the surface of the film. As the film is moved horizontally, the drag communicated to the knife edge causes the lever to describe an arc. The angle increases to a maximum and remains constant while a film of definite width is stripped off. A repeat run over the bare metal enables a blank evaluation of the metal-to-metal friction, and the stripping force is obtained by difference. Results are calculated in dynes/cm., and are independent of the load on the knife edge.

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## SOLVENTS (H. L. Howard, B.Sc., A.R.C.S., D.I.C., M.I.Chem.E., F.R.I.C.)

### *Hydrocarbons*

THE production of toluene from petroleum by high-temperature cracking and hydrogenation processes has caused difficulties in obtaining satisfactory compliance with specifications in respect of acid-wash colour, and materials, initially satisfactory, have been found to deteriorate rapidly on storage. P. L. Brandt, R. J. Lee, and F. T. Wadsworth<sup>1</sup> have traced this defect to the presence of conjugated di-olefins such as 2-methylpentadiene and cyclopentadiene. Mono-olefins produce no effect, whereas relatively small amounts (below 0.01%) of di-olefins produce considerable discoloration. Treatment with maleic anhydride in very small amount at 100° F. was surprisingly effective and also notably improved stability on storage. Refluxing over a solid catalyst consisting of phosphoric acid absorbed on kieselguhr was also effective. Both these methods eliminate the necessity for acid washing, but do not remove mono-olefins. Advantages, principally in respect of odour and improved volatility, resulting from the use of de-polarised petroleum naphthas are stressed by C. Allen.<sup>2</sup> The use of chemical stimulants to increase the exudation of oleo-resin from the Slash and Longleaf pines is shown to be without deleterious effect on the turpentine or rosin produced, nor do they influence the ratio in which these products are formed.<sup>3</sup>

### *Furan solvents*

The spectacular development of a whole range of solvents resulting from the original project of utilising waste oat husks for the production of furfuraldehyde is described by H. J. Brownlee and C. S. Miner.<sup>4</sup> Production has so far outstripped the availability of the original waste material that recourse must now be had to other similar materials, and the number and complexity of the products has led to the development of a valuable range of solvents and chemical intermediates. G. F. Wright and H. Gilman<sup>5</sup> have surveyed the methods available for the production of substituted furans. Mild conditions are desirable in view of the reactivity of furan by comparison with corresponding benzenoid compounds. 1 : 4 Addition reactions of the Diels-Alder type occur with ease, ring closure of the corresponding 1 : 4-di-ketones is often utilised and various cyclisation reactions may be employed. Patents have been granted for the production of alcohols<sup>6</sup> from substituted furans by hydrogenation under pressure at 200/300° C. and for the halogenation<sup>7</sup> of substituted tetrahydropyrans.

### *Nitro-compounds*

Systematic investigation of the production of new nitro-compounds previously noticed (see 1947 Report) continues. 1 : 2-Dinitro-2 : 4 : 4-trimethylpentane may be obtained from the corresponding olefin along with nitro-alcohols and their nitrates by the action of nitrogen peroxide.<sup>8</sup> Nitro-nitroso compounds may be converted into di-nitro compounds

by the same means.<sup>9</sup> Oleic acid under similar conditions yields a mixture of dinitro- and nitro-hydroxy-heptadecane carboxylic acid.<sup>8</sup> 1:3-Dinitro-2:2-dimethylpropane and its analogues have been prepared.<sup>10</sup> by allowing primary nitroparaffins to react with substituted 2-nitroethyl-alcohols in the presence of piperidine. By the reaction under pressure of nitrogen peroxide with nitro-alcohols the corresponding nitric esters are obtained.<sup>11</sup> Nitro-olefins may in turn be obtained from dinitro-paraffins by treatment with ammonia in the presence of a suitable solvent under anhydrous conditions,<sup>12</sup> or in the presence of water.<sup>13,14</sup> Nitro-alcohols may be converted into nitro-olefins by heating with phthalic anhydride,<sup>15</sup> and esters of  $\beta$ -nitro-alcohols undergo pyrolysis in the presence of salts of alkaline earths yielding nitro-olefins.<sup>16</sup>

### Analysis

The accuracy of the acid solubility test for olefins and aromatics is increased<sup>17</sup> by first dissolving the hydrocarbon in glacial acetic acid and then adding 15% fuming sulphuric acid. The bromine number is found to be a reliable index of olefin content and discrepancies between it and the acid solubility test are attributed to incomplete solution of some olefins in 98% sulphuric acid as well as partial solution of some of the saturated compounds. An improved technique for the determination of bromine number is proposed by H. L. Johnson and R. A. Clark.<sup>18</sup> The determination of olefin content by means of nitrogen tetroxide has been investigated by a group of A.S.T.M. co-operators,<sup>19</sup> who conclude that this method is fundamentally more reliable than the bromine number determination. C. E. A. Shanahan<sup>20</sup> proposes a simple and rapid method for the analysis of mixtures of toluene, *n*-butyl alcohol, and water. The mixture is titrated with water until phase-separation occurs, followed by determination of the refractive index of the predominant phase. Reference to two graphs enables the complete composition of the ternary mixture to be ascertained. Minute traces of water in gases and liquids may be determined by means of infra-red spectroscopy.<sup>21</sup> Absorption in the  $2.67\ \mu$  water-band is measured and the method is particularly applicable to refrigerants. It is satisfactory for carbon tetrachloride, tetrachlorethylene, and trichlor-monofluoromethane (Freon-II), but interference within this region precludes its use for many similar liquids, including chloroform. The determination of alcoholic hydroxyl by means of phthalic anhydride in hot pyridine solution yields satisfactory results with primary and secondary alcohols.<sup>22</sup> Good results are obtained with aqueous solutions and with low boiling alcohols. Phenols do not react and aldehydes do not interfere. An apparatus has been devised by the Shell Development Co.<sup>23</sup> for the determination of evaporation rate curves of solvents under conditions of constant temperature and humidity.

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# RUBBER

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AS the detailed comment which follows indicates, the major fields of interest in the period covered by the review have been latex and raw rubber. This is not surprising. There has been a considerable expansion in the manufacture of the so-called foamed latex, particularly as an upholstery material in transportation, and still greater developments have been forecast. The use of synthetic latexes for this type of production presented many problems during the war, but there is obviously a considerable advantage in using a material which can be produced at or near the manufacturing units as compared with the cost of concentrating and transporting natural latex.

In the raw rubber field, intensive work has been carried out on the production of polymers having better technical properties than the general purpose synthetics which had to be produced under war emergency conditions, and a marked step forward has been made by carrying out the polymerisation at lower temperatures. Although the advantages claimed for these new polymers have not yet been completely established, it is significant that a considerable expansion in production has recently been announced.

During the war period efforts were made to forecast the possible world consumption of raw rubber (both natural and synthetic) under post-war conditions. The estimates made varied between one and a half and two million tons per year as compared with a figure of approximately one million tons just prior to the war. Figures for the first nine months of 1948 show an annual rate of consumption of the order of 1,750,000 tons. The output of natural rubber for the same period was at the rate of 1,500,000 tons, the output of synthetic rubber being approximately 500,000 tons. Whereas the output of natural rubber was some 200,000 tons higher than for the corresponding period in 1947, the consumption was slightly lower, mainly due to a falling off in the amount of rubber required for transportation purposes.

To help the coal position in Western Germany the manufacture of Buna S has been suspended, so that Germany once again appears in the list of countries consuming appreciable amounts of natural rubber.

The marked increase in the use of latex is shown by figures published for the first nine months of 1948. The U.S. consumption of natural latex is given at the rate of 22,730 tons a year, the annual production figure for GR-S latex being approximately 21,700 tons. The figure for natural latex consumption in the U.K. is about 9,250 tons a year.

## Latex

The intensive research on synthetic rubbers which continues to be carried out, mainly in the U.S.A., has again given rise to warnings as to the possibility of these materials coming into serious competition with

the natural product both on economic and technical grounds. With regard to the latter, in a general review, on the preparation of natural rubber latexes, E. M. McCollm<sup>1</sup> suggests that there is some slight evidence indicating that the rubber molecule may still be growing in size at the time the latex is tapped. If such evidence is valid, the author considers that it may be found possible to continue polymerisation under controlled conditions outside the tree and thus obtain an even larger and presumably stronger molecule. Reasonable prospects of improving the rubber hydrocarbon are also suggested by the author from the marked increase in plasticity of the rubber after autoclaving latex with 2% potassium hydroxide for one hour at 10 lb. steam pressure excluding air, from the decrease in plasticity on keeping quadruply centrifuged ammoniated latex, and from the increased resistance of rubber to solvents when the latex from which it is separated has been kept for about two months.<sup>2</sup>

An examination into the action of latex preservatives has shown that in some instances ammonia has a deleterious effect on the latex and attempts have therefore been made to find a suitable alternative. In this connection chlorinated phenols have been indicated as showing considerable promise.<sup>3</sup> Ammonia and formaldehyde are still, however, the most important materials used for this purpose, and the following patents involving their use may be selected from those appearing in the year's literature. According to one process, treatment with formaldehyde is followed by the addition of ammonia so that there remains no substantial excess of free formaldehyde to form a rubber accelerator *in situ*.<sup>4</sup> Latex can also be preserved with 0.2–0.3% formaldehyde, allowed to age for three days, and sufficient alkali added to raise the  $p_H$  value from 6.5–11.0. The latex is then diluted to less than 20% solids content and the cream and serum portions separated.<sup>5</sup> In an analogous process, the formaldehyde is allowed to act completely before the addition of ammonia. This method is claimed to yield a rubber resistant to swelling and water and with improved milling properties.<sup>6</sup>

Factors affecting the stability of *Hevea* latex have been reviewed by F. J. Paton,<sup>7</sup> who points out that changes after the latex has been concentrated and preserved are determined by rapid alterations occurring between tapping and centrifuging. A more general account of colloidal stability has been presented by E. G. Cockbain,<sup>8</sup> who starts from the standpoint that the stability of latex depends ultimately on the properties of the interfacial film surrounding the particles. Factors responsible for stabilisation are considered on the basis of the electric charge on the particles; the degree of hydration; interfacial tension, viscosity, elasticity, and plasticity; and the influence of the lipid layer. Attempts to correlate the findings with the phenomena of creaming, thickening, gelation, flocculation, and coagulation are necessarily incomplete as different theories of creaming and gelation are still held.

An evaluation of creaming agents has been made by W. S. Davey and K. C. Sekar,<sup>9</sup> in which the authors review the various agents, practical developments, and methods of test, and possible explanations are offered to account for the differences encountered by manufacturers between creamed and centrifuged concentrates. The same authors have also dealt with the mechanism of creaming,<sup>10</sup> and conclude that the theory

involving the adsorption of the creaming agent on the rubber particles is inconsistent with available experimental evidence. It is suggested that the creaming agents act by desolvating (*i.e.*, dehydrating) the protein protective layer, thereby reducing repellent forces between the particles.

The different effects of creaming and centrifugal separation on the final product have also been discussed in a German paper,<sup>11</sup> and the possibility is pointed out of obtaining latices suitable for various purposes by mixing concentrates obtained in various ways. Mention may also be made here of the purification and concentration of latex by the electro-decantation process. This has been described by H. P. Stevens,<sup>12</sup> who states that the resulting concentrate is purer than that obtained by creaming and is comparable to the centrifuged product.

Fractionation by centrifuging has been used to produce a series of latexes each having a definite average particle size.<sup>13</sup> Control is affected by varying such factors as speed of operation and the distance between the plates in the centrifuge. The centrifugal separation of latex into a heavy yellow and a lighter white fraction has been described by L. N. S. Homans and J. W. van Gils<sup>14</sup> in an account of war-time research carried out by the Dutch Indies Rubber Research Institute and in a later paper<sup>15</sup> the same authors examine the two dispersed "phases" of the *Hevea* system with special reference to the lutoids and their importance in relation to the general properties of the latex. Changes in the non-rubber ether-soluble part of ammoniated latex have been examined analytically<sup>16</sup> over a period of 15 months storage, after which period the acid and saponification values appear to indicate that the latex still contains unhydrolysed saponifiable compounds. It is suggested that this may be due to the presence of waxes and sterol esters which are known to be stable against chemical saponification agents such as ammonia.

Factors influencing the spontaneous coagulation of latex continue to be studied and in a discussion on the effect of sodium soaps and the rôle played by magnesium and calcium ions, G. E. van Gils<sup>17</sup> concludes that spontaneous coagulation does not result from the formation of acidic substances. The coagulation of preserved latex by sodium silicofluoride forms the subject of a paper presented to the Rubber Technical Conference, London, by E. A. Murphy, E. W. Madge, and D. W. Pounder.<sup>18</sup> The authors describe extended experimental work on gelling behaviour as exemplified by the  $p_H$  at which gelling takes place and the influence of zinc oxide and surface-active substances is discussed. It is suggested that the gelling action may be due to formation of silicic acid. A method of sensitising rubber latex to make it capable of being coagulated by heat alone and involving the addition of an aqueous suspension of colloidal zinc oxide has been patented,<sup>19</sup> and an interesting article by F. Lepetit<sup>20</sup> gives an account of the attempts made to find an alternative method to heat sensitisation with ammonium salts.

The increasing interest in continuous coagulation has again been emphasised by H. P. Stevens<sup>21</sup> in a paper in which methods are examined in relation to such questions as accelerating coalescence, the double phenomenon of minute aggregates or flocs followed by their coalescence and the adjustment of coagulation, and details have also been given<sup>22</sup>

of a process involving the use of straight-chain fatty acids, certain phenols or higher fatty alcohols and the adjustment of the  $p_H$  to 4.5-4.9.

Natural anti-oxidants in fresh *Hevea* latex have been isolated<sup>23</sup> by separating the latex into water-soluble and ether-soluble fractions which were again separated into sub-fractions, each sub-fraction being tested for its anti-oxidant action on crude and vulcanised rubber. All the water-soluble fractions and a few of the ether-soluble fractions (e.g., lecithins) show a protective action. The same investigator has also described<sup>24</sup> the natural accelerators in latex. These are certain nitrogenous bases which have been isolated and compared for accelerating power with M.B.T.

The growing importance of wetting agents and detergents in industry and the general theory underlying their use have been outlined by E. S. Paice,<sup>25</sup> and the relationship between the chemical structure and performance of surface active agents has been discussed by W. D. Scott and D. S. P. Roebuck,<sup>26</sup> who deal with the mechanism of wetting and penetration in relation to sulphates, carboxylates, sulphonates, cationic hydrophilic groups, and non-ionic hydrophilic and hydrophobic groups. A sulphuric acid reaction product of 2-mercapto-4:6:6-trimethylthiazine has been advocated as a useful wetting agent,<sup>27</sup> and a review has been given of German soapless detergents.<sup>28</sup> Ethylene oxide condensation products were used as the best synthetic detergents manufactured in Germany.

A few miscellaneous items may be touched upon here of interest in connection with latex compounding. In a method for dispersing anti-oxidants in latex a master latex is produced by melting together 2:2:4-trimethyl-6-phenyl-1:2-dihydroxy quinoline and diphenyl *p*-phenylene diamine and then adding a soap formed from triethanolamine and oleic acid. The molten mass is added to a hot solution of ammonium caseinate.<sup>29</sup> An aqueous emulsion of a cracked gasoline distillate polymer has been advanced as a latex extender,<sup>30</sup> and a latex thickener based upon acrylate co-polymers is said to provide higher viscosities at lower concentrations than is the case with most commercial thickeners.<sup>31</sup> Finally, the use of Pliolite 109, mentioned in last year's report, has again been noted, particularly in regard to its capacity for improving stiffness, hardness, and tear strength when incorporated in natural latex.<sup>32,33</sup>

In the field of synthetic latex a process has been evolved for the production of stable synthetic latexes of 55-60% total solids direct from the reactor.<sup>34</sup> It is claimed that the average particle size approaches that of natural latex and the mechanical stability is said to be excellent.

Details have also been given of a new polymer (GR-S 65) having a water absorption lower than that of the natural product.<sup>35</sup> In this instance the latex is introduced below the surface of the acid coagulant with the simultaneous admission of air and in the presence of a protective agent such as glue.

The rôle of aggregating conditions and particle fusion in the growth of polymer particles has been investigated, and results appear to indicate that the particle size of a latex formed by emulsion polymerisation is determined almost entirely by the stabilising capacity of the medium.<sup>36</sup> A number of methods have been advocated for increasing particle size.

A dilute aqueous solution of an ionisable salt such as sodium chloride may be added in amounts insufficient to cause coagulation, and the latex then heated to 50–100° C. for about two hours. It is claimed for this method that stability is increased and thicker films can be deposited.<sup>37</sup> In controlling conditions of emulsion polymerisation it has been found that average particle size can also be increased by reducing the soap content in the initial charge, but no difference in the properties of the vulcanisate attributable to the increased particle size can be discovered.<sup>38</sup>

A substantial amount of work has been reported during the year on the creaming of synthetic latexes and a process has been developed for creaming butadiene–acrylonitrile co-polymers involving de-stabilisation with an inorganic salt, re-stabilisation with an inorganic or organic base and the addition of a creaming agent,<sup>39</sup> while another method has been described by which aqueous emulsions of butadiene–1 : 3 polymers and co-polymers are creamed in the presence of a hydrophilic, colloidal creaming agent, and 0.4–0.3% of a strong alkali.<sup>40</sup> Among the processes based on lowering and increasing the  $p_H$  value prior to the addition of a hydrophilic creaming agent, mention may also be made of a method in which these alterations in  $p_H$  value are made in the presence of small proportions of glue.<sup>41</sup>

A comprehensive survey of the many and varied industrial applications of latex does not perhaps fall within the scope of the present review, but attention may be directed to one or two typical lines of development. In a series of papers on latex processes and potentialities, W. H. Stevens<sup>42</sup> has surveyed the production of solid articles by moulding and casting, cement–latex compositions, the application of latex to fibres and the development of modified latexes, and a great deal of attention has been directed towards the production of dried latex films and coatings.<sup>43,44,45</sup>

The general principles underlying the drying of latex articles have been outlined by E. O. Partridge and M. E. Hansen,<sup>46</sup> special attention being given to problems arising from the effect of relative and absolute humidity, temperature, and air circulation on the finished product. The application of high frequency–dielectric heating has also been found to expedite drying in the dipping process.<sup>47</sup>

The development of the use of rayon cord for tyres has been mentioned in the last two reports. The behaviour of the cord during latex dipping has now been examined and comparisons made with cotton,<sup>48</sup> and a dye–staining technique has been developed for determining the degree of latex penetration into the tyre cords.<sup>49</sup>

### Raw rubber

Although there is no present or potential source of natural rubber likely to compete seriously with *Hevea*, research continues to be made on rubbers of different origin. Interest has been directed mainly towards guayule rubber, and detailed accounts have been given of its characteristics and methods of preparation.<sup>50,51</sup> *Cryptostegia grandiflora*,<sup>52</sup> golden rod,<sup>53</sup> and *Euphorbia* resins<sup>54</sup> have also received further attention. The possible methods of evaluating and grading wild rubbers have been reviewed,<sup>55</sup> mainly in relation to rate of vulcanisation and plasticity characteristics,

and a comparative examination of different species of *Hevea* has been made by G. J. van der Bie, who comments on the paucity of published data on the selecting of rubber trees to give rubbers with specific qualities.<sup>56</sup> Investigations carried out prior to the war on the variability of crude rubber have been published during the year, including an account of the isolating of fractions of non-rubber substances from fresh, unpreserved latex and their effect on the vulcanising behaviour of purified rubber.<sup>57</sup>

De-proteinised or otherwise purified rubbers have been the subject of some study. G. Martin<sup>58</sup> has reviewed the preparation and properties of a rubber with 99.9% pure hydrocarbon which has shown marked improvement in resilience and earlier work on low protein rubbers has been published by the Rubber Research Board.<sup>59</sup> Mechanical, ageing, hygroscopic, and electrical properties of purified rubber vulcanisates have been studied by J. R. Scott,<sup>60</sup> who has found no inferiority in mechanical properties as compared with normal crêpe and smoked sheet. Poorer ageing, however, was shown with accelerators having no anti-oxidant effect and electrical tests indicated no improvement in permittivity, but power-factor and loss-factor, on the other hand, showed signs of improvement. Other electrical properties have been tabulated and the patent literature summarised.<sup>61</sup>

An inquiry into the influence of the presence of strong acids on the durability of crude rubber has confirmed<sup>62</sup> the detrimental effects of excess hydrochloric, sulphuric, and nitric acids. Formic, oxalic, and tartaric acids have proved entirely harmless, phosphoric acid, and alum being intermediate in effect.

A general account of the causes and determination of the oxidisability of rubber has been given by J. Le Bras,<sup>63</sup> who describes a method of determination using a glass manometer. The test results are correlated with those obtained with the Geer oven. The method is further elaborated by the same author in a paper dealing with the kinetic study of the oxidation of raw rubber.<sup>64</sup> The difficulty of obtaining reproducible quantitative results is emphasised together with the effects of storage, partial pressure of the oxygen, and the rubber concentration. The difference in the behaviour of anti-oxidants and oxygen deactivators is demonstrated, the former showing little influence, while the latter remain effective.

At the International Rheological Conference, held in Holland during September, 1948, several papers were presented of interest to rubber technologists. Rheological phenomena encountered in industrial processes were reviewed by R. Houwink,<sup>65</sup> special consideration being given to viscosity coefficient and yield value and an account was given<sup>66</sup> of the continuum theory of the elasticity of volume and form in which sponge rubber was used to demonstrate experimentally the effects which are to be expected in accordance with the general laws of the theory. The view is expressed that a wide range of structures of cellular or fibrous type may provide models for the hidden molecular structure of the apparently continuous colloidal solutions in the shear-elastic class.

A comprehensive scheme dealing uniformly with all macroscopic aspects of rheological behaviour was developed by K. Weissenberg,<sup>67</sup> and

the use of the rotation viscometer in studying the properties of unvulcanised rubber was evaluated by G. G. H. Hamm and A. van Rossem,<sup>68</sup> who demonstrated that there is no "yield-point" with masticated rubber. In this connection mention may be made of a paper by E. K. Fischer and C. H. Lindsley,<sup>69</sup> in which details are given of the application of the rotating-cylinder viscometer in relation to retarding torque, the determination of the magnitude of end traction on the inner cylinder, and the variation in the rate of shear between the cylinders.

Data on the relation between rate of flow and shear stress at various temperatures have been given by D. W. Saunders and L. R. G. Treloar,<sup>70</sup> the flow curves being obtained from natural rubber using the Piper and Scott modification of the Mooney viscometer, and a comparison is made with the Ostwald-de Waele relations used by J. R. Scott and others. Among the papers relating to plasticity tests, a comparison has been made by R. G. Newton, J. R. Scott, and R. W. Whorlow<sup>71</sup> between the power of different plastimeters for discriminating between samples of various types of rubber. Defo and Hoekstra instruments for example are preferable to the Williams test in discriminating between samples of smoked sheet masticated for different periods. The authors, however, underline the fact that discrimination depends upon the purpose for which the results are required as well as upon the kind of rubber concerned. In a review of the development of plasticity tests, R. W. Whorlow<sup>72</sup> has discussed the principal types of compression plastimeter, and expresses the opinion that attempts to improve the original Williams technique have not in general been successful.

A few miscellaneous items connected with the examination of raw rubber may conveniently be included in this section. Improved X-ray techniques have been used in the examination of rubber and gutta-percha and the comparative degree of crystallinity established.<sup>73</sup> The highest figure obtained for raw rubber was 38% on a 29-year-old sample, but generally the percentage for rubber is lower than this. The degree of crystallisation for gutta-percha is given as 45-50%. The relation of crystallisation to vulcanising period, elongation, and temperature is investigated and the results obtained show a high measure of agreement with other experimental evidence. The application of infra-red spectroscopy to the examination of rubber has been described, and details given of the bands in the spectrum. An interesting possibility mentioned by the author is the determination of molecular weights of polymers by measuring the ratio of the number of groups to the number of monomer units.<sup>74</sup>

Factors relating to the swelling of high molecular substances (including rubber) in liquids have been considered by J. J. Hermans,<sup>75</sup> with special reference to recent work on the thermodynamics of gels subjected to stresses. Almost all thermodynamic relations in this field are simple if expressed in terms of force and displacement instead of stresses and strains. The author also discusses the problem of accounting for the fact that the orientation of the structural elements in a gel is a function of its co-ordinates and assumes that the gel, although anisotropic as far as its swelling tendency is concerned, is isotropic in its response to small stresses.

### Rubber derivatives and synthetic materials

The investigation and preparation of new rubber derivatives of possible commercial interest have continued to receive attention during the year. In this connection the reaction of thiols and thiolacids with rubber and allied compounds are reviewed, as they seem to offer a means of introducing various groups along the polyisoprene chain with the probability of preserving the molecular character of the original polymer.<sup>76,77</sup>

Numerous compounds have also been described which are of interest in the formulation of chemical resistant paints and wrapping films,<sup>78,79,80,81</sup> and a fundamentally new process for the preparation of rubber hydrochloride from latex stabilised with cationic or non-ionic emulsifying agents has indicated that the hydrochlorination of latex is not accompanied by cyclisation.<sup>82</sup>

Considerable work on the improvement of anti-fouling compositions based on chlorinated rubber has been published and a review of researches carried out by the Marine Corrosion Sub-Committee of the Iron and Steel Institute indicates the suitability of chlorinated rubber as the medium, with basic lead sulphate as the pigment.<sup>83</sup> The inclusion of chlorinated rubber in an alkyd resin paint reduces the drying time by 50%.<sup>84</sup>

The desirability of chlorinated rubber as a vehicle for toxic agents is stated to be due to its inherent immunity to certain marine species and the ease with which anti-oxidant toxic agents can be incorporated.<sup>85</sup> The behaviour of these paints at high temperatures however has been reported as not good.<sup>86</sup> An exhaustive review of the manufacture and use of chlorinated paints in Germany has also been made available.<sup>87,88</sup>

A comparatively new field for anti-fouling compositions where the normal paints are unsuitable is on the hulls of flying boats. Here, the weight, brittleness, lack of smoothness and corrosive tendencies on aluminium alloys of the older compositions have presented many difficulties, and investigations are reported which have resulted in the formulation of efficient films no more than 2 mils. in thickness.<sup>89</sup>

An interesting chlorinated product containing up to 50% chlorine is stated to be made in an elastic form resembling natural rubber but more oil-resistant. This is carried out by mixing sulphuryl chloride with a solution of rubber, balata, or gutta-percha at low temperatures and then heating the mixture to the reaction temperature while removing the reaction products with a stream of an inert gas.<sup>90,91</sup>

Early this year, the American synthetic rubber industry announced the development of a new type of GR-S with properties better than natural rubber and speculations on its potentialities have been somewhat unrestrained. The new rubber is made by reducing the temperature of polymerisation to 5° C. (41° F.) and by the development of special types of accelerators and "stoppers." A review of the experiments leading to the successful large-scale production of "cold" GR-S also contains hitherto unpublished data on the standard GR-S process.<sup>92</sup> Of great interest to chemists is the method employed to overcome the increase in reaction time due to the reduced temperature. The most successful method of bringing this back approximately to the original time of 12-18 hours is the so-called "Redox" system of catalysis, in which both

a reducing and an oxidising agent are employed. In the early work benzoyl peroxide was used as the oxidising agent and sugars, salts of heavy metals, etc., used as the reducing agents. Later systems employ M.D.N. (diazo-2'-naphthyl ether)—ferricyanide activators or cumene hydroperoxide. Polymerisation at low temperature tends to give a polymer having long chains and reduces the risk and frequency of cross-linkages. The technical properties of the vulcanisate have been stated to show equivalent advantages; it has been reported, for example, as having higher tensile values at ordinary and elevated temperatures and higher resilience and flexing life. Some recent results indicate that carbon black can be incorporated faster than is the case with normal GR-S or natural rubber, and extrusion is carried out at a faster rate and gives a smoother extruded appearance.<sup>93</sup> These improvements have been confirmed by road tests on tyres which gave better tread life and freedom from tread cracking or cut growth,<sup>94</sup> and it is interesting to note that the end of the year saw "cold rubber" tyres being made on the regular production line. A comprehensive review of the properties and future prospects of this type of material in comparison with natural rubber has recently been published.<sup>95</sup>

Although the announcement of the developments in "cold rubber" has tended to focus interest on this type of product, development work on the large range of copolymers of the GR-S type has been steadily advancing, and a timely survey and discussion of the development, merits, and improvements of the butadiene-styrene and isoprene-styrene polymers have appeared from the Office of Rubber Research, Washington.<sup>96</sup> Comparison between natural and GR-S rubbers indicates an improvement in quality and uniformity, and the importance of careful compounding with fine pigments is emphasised to obtain the best results from GR-S. Even under the best conditions however GR-S suffers from heat shortening at elevated temperatures, a disadvantage not found in the natural product.<sup>97</sup>

High styrene co-polymers, based on the normal GR-S recipe but with the proportions approximately reversed, are becoming increasingly popular in the U.S.A. for the manufacture of non-marking shoe soles. Their use is claimed to improve processing properties, to remove the rubbery feel, and be more abrasion resistant.<sup>98</sup> A mixture of high styrene polymers with natural rubber is claimed to give very desirable characteristics, including high tensile and high abrasion resistance with improved ageing properties.<sup>99</sup>

The search for better polymerisation accelerators continues, the main objective being the reduction of the time of processing and the improvement of the homogeneity of the final product. Derivatives of dodecylthiol, for example, have been prepared which slowly liberate the thiol during polymerisation, the object in this case being to obtain a polymer in which the molecular weight does not vary as a function of conversion.<sup>100</sup>

The "Redox" system operating at normal temperatures and using benzoyl peroxide and ferrous sulphate has been discussed and the various techniques described.<sup>101</sup> Various benzoyl disulphide analogues have been examined in this connection and have been reported to be as effective as dodecylthiol but are not at all comparable as chain transfer agents.<sup>102</sup>

Rubber-like polymers containing fluorine, first introduced in 1947, have been further developed to increase their high resistance to oils and resilience at low temperatures.<sup>103,104</sup> Good freeze resistance is also claimed for a neoprene mixed in the emulsion stage with polybutadiene,<sup>105</sup> and for a polychloroprene modified with special wax.<sup>106</sup>

Silicone rubber continues to attract attention for applications where high or low temperature resistance is of fundamental importance. Data to show the effect of prolonged exposure to temperatures up to 482° F. and down to - 80° F. have been reported,<sup>107</sup> and improvement in heat resistance is claimed by treatment with chlorine compounds with the addition of litharge.<sup>108,109,110</sup>

Further developments on "Lactoprene" rubber, mentioned in last year's report, have been published and various chlorine-containing ethyl acrylate co-polymers prepared which vulcanise satisfactorily and indicate the usefulness of the halogen atom for vulcanisation purposes. The different co-polymers show variation in moulding characteristics, rate of cure and properties of vulcanisates. The 2-chloroallyl co-polymer vulcanises most rapidly and the 95% ethyl acrylate-2-chloroethyl vinyl ether co-polymer (Lactoprene-EV) yields vulcanisates with outstanding resistance to oils, oxidation and heat ageing.<sup>111</sup>

A process is claimed for co-polymerising vinyl chloride and acrylonitrile. Polyvinyl chloride is almost insoluble, and polyacrylonitrile is completely insoluble, in acetone; the co-polymer, however, is soluble.<sup>112</sup>

Finally, before leaving the subject of synthetic materials, attention should be drawn to the publication during the year of a B.I.O.S. Overall Report in which T. R. Dawson gives a systematic survey of the information available in the numerous reports issued on the German rubber industry. These relate mainly to the Buna-S and Perbunan types of synthetic rubber.<sup>113</sup>

## Compounding materials

Carbon black retains its place as the most effective reinforcing agent and small scale experiments in its manufacture from various residues of the gas and petroleum industries in the U.K. have been described.<sup>114</sup> Electric furnaces (originally designed for making magnesium) are being used for turning imported oils into blacks, although it is intended to use oil from Scottish coal as soon as possible.<sup>115</sup>

The change over to furnace type blacks in the U.S.A. has resulted in many publications demonstrating their general properties. R. L. Carr and W. B. Wiegand have sketched in the historical background which influenced the change over from channel blacks and have compared the physical properties and processing differences of the various blacks.<sup>116</sup> The greater relative importance of structure and  $p_H$  on processing, vulcanising and physical properties has been discussed,<sup>117</sup> while a modification in compounding technique is stated to be necessary due to the different effect on the rate of vulcanisation as compared with channel blacks.<sup>118,119</sup> The superior reinforcing properties of high abrasion black (HAF) are illustrated in "bound" rubber figures which show that it not only attracts more rubber to its surface, but holds it more tightly than

E.P.C. black.<sup>120,121</sup> An extrusion shrinkage test has been reported as useful for judging processing properties of the various furnace blacks.<sup>122</sup>

A novel hydrophilic black of value as a reinforcing agent for synthetic rubber by incorporation in the latex has been patented. The process is carried out by combining the desired black with sodium hypochlorite at a controlled  $p_H$  and drying the resultant product at below 100° c.<sup>123</sup>

The search for improved softeners to aid the processing of GR-S combined with the cheapness and availability of petroleum and its by-products has initiated several interesting papers on the evaluation of petroleum products for the rubber industry. The higher boiling fractions of crude petroleum oil consist of five basic groups of components, each capable of being identified and quantitatively determined by chemical analysis and each group shows typical behaviour in test compounds. These tests have revealed the possibility of predicting the performance of the petroleum products without resort to mixing and testing a rubber compound.<sup>124</sup> The methods of analysis are reported in detail.<sup>125</sup>

A comprehensive paper by Rostler and Pardew describes the background of petroleum products for rubber, their history, composition, classification, and properties.<sup>126</sup>

An attempt has been made to correlate the hardness of a vulcanisate with its filler content through a mathematical expression. The experimental results obtained with carbon black and calcium carbonate agree well with the values predicted mathematically, and the hardness is stated to depend essentially on the percentage loading and particle shape only.<sup>127</sup> A discrepancy noted at very low loadings in natural rubber appears to be due to the effect of pigment in breakdown of the rubber. This latter is considered more important for plasticity than for properties of vulcanised rubber, which fact explains some of the difficulty previously encountered in interpreting plasticity results.<sup>128</sup>

## Vulcanisation

An infrequently discussed aspect of vulcanisation control is the effect of moisture, both in the rubber and the pigment. A serious proposal has been put forward for the complete humidity control of pigment storage and a different approach—that of developing a vulcanising recipe, insensitive to moisture in the compounded stock—has been suggested. A successful accelerator combination has also been given with the range of moisture content to which it is insensitive.<sup>129</sup>

The tendency towards higher mixing speeds, with the consequent development of higher temperatures in the pre-vulcanisation stages of manufacture, has promoted an investigation into the stability of accelerators at temperatures up to 350° F. All accelerators show some impairment in strength but thiazoles, thiazole derivatives, and activated thiazoles are considered satisfactory. Thiourams and dithiocarbamates lose considerable accelerating value.<sup>130</sup>

Radio-frequency curing of rubber and plastics has continued to attract attention, and a critical review of the possibilities and limitations of the method has been published.<sup>131</sup> The author considers that the amount of time saved by the use of high frequency for pre-heating is small compared with the saving which may be realised by its application to the

full curing cycle. The amount of radio-frequency utilised in the rubber industry, however, will remain relatively small compared with other forms until information is available on suitable high-pressure mould dielectric materials. A comparison of vulcanisates prepared from a rubber stock by conventional steam methods and by radio-frequency heating under equivalent conditions of time and temperature showed no significant differences.<sup>132</sup> Experiments at very high curing pressures have also been carried out and more resilient stock with an increased electrical resistivity claimed.<sup>133</sup>

The application of the Peachey process to various synthetic rubbers has been investigated. All types gave good vulcanisates except GR-M, but no synthetic cured more rapidly than natural rubber.<sup>134</sup>

Although sulphur is used almost universally as a promoter of vulcanisation, the special properties of selenium for the same purpose still claim interest and a recent patent indicates a novel approach to its application in solution form, whereby a vulcanisate is produced at normal atmospheric temperatures. This development has distinct interest in the adhesive field.<sup>135</sup>

### Vulcanised rubber

The extensive work which has been carried out on the examination of the structure and mechanical properties of vulcanised rubber has resulted in a number of papers in which attention is directed mainly towards thermodynamic theory and elasticity. For example, an outline of the modern thermodynamic theory of rubber structure has been given by E. F. Powell<sup>136</sup> in an attempt to show how the conception of a network of randomly-linked molecules can explain many of the unique characteristics of rubber behaviour. The author also examines the effect of heat and extreme cold on hardness and resilience. A typical representation of rubber-like elasticity has been developed by K. Wolf<sup>137</sup> in which the elastic body is made up of a system of partially mobile chains joined by their ends to others to form a three-dimensional network that permits elongation. The length of the chains, their mobility and elastic recoil are considered and a definition given of the rubber-like state. The dependence of elastic properties on the degree of cross-linking has also been discussed,<sup>138</sup> and in work carried out on azo-vulcanised rubber the magnitude of the elastic modulus has been found to be in agreement with the theory which relates the force of retraction at a given elongation to the degree of cross-linking.

Experiments carried out on the effects of stretching have indicated that the properties of pure vulcanisates are only slightly affected by previous stretching or flexing, while a considerable change is recorded in the case of reinforced rubber in which the increase of stiffness, electrical conductivity and power factor produced by the incorporation of fillers are destroyed, presumably owing to the breakdown of both agglomerates and chains of the filler particles and the adsorption of the filler particles on the rubber.<sup>139</sup> Stretching characteristics, high-elastic deformation and hysteresis have also been examined and their importance assessed in the application of rubber for such articles as vibration insulators and shock absorbers,<sup>140</sup> while the applications of elasticity theory to rubber

engineering have been reviewed by R. S. Rivlin.<sup>141</sup> The same author has studied the large elastic deformations of isotropic materials,<sup>142</sup> and the deformation characteristics of rubber compounds have been examined as a possible measure of quality.<sup>143</sup>

In a paper on the dynamic mechanical properties of rubber-like materials, A. W. Nolle<sup>144</sup> has described a method whereby the differential dynamic Young's modulus has been measured over a frequency-temperature range of from  $10^{-1}$  to  $10^5$  cycles per second and from  $-50$  to  $100^\circ\text{C}$ . and the dynamic modulus results obtained by the author in the limiting case of very low frequency below the range of appreciable relaxation efforts are shown to be in agreement with the kinetic theory of rubber-like elasticity. An examination of the stresses and birefringence in rubber subjected to general homogeneous strain has also been made,<sup>145</sup> and it has been found that the stresses cannot be accurately represented by the equations derived from the network theory, a closer approximation being given by the general theory of Mooney. A visco-elastic study of modulus in rubber vulcanisates has been described by L. T. Eby and D. J. Buckley in which the elastic and viscous components have been separated to facilitate the study of the effects of compounding and vulcanisation variables,<sup>146</sup> and an investigation of the free retraction of elongated rubbers has been carried out in which elasticity is judged in terms of speed of retraction and permanent set.<sup>147</sup>

A certain amount of interest has been shown during the period under review in the photo-elastic phenomena exhibited by natural rubber and other elastomers and a paper by G. F. Morton<sup>148</sup> emphasises the relationship shown between the principal stresses in a two-dimensional stress system and the interference pattern produced by passing polarised light through a loaded transparent model. Direction and magnitude of shear stress are obtained directly from the fringe patterns, and examples are given to demonstrate the simplicity of the photo-elastic method as compared with the mathematical approach. The change in birefringence as a function of time and elongation has been studied in various elastomers and the differences shown have been explained in the light of the degree of crystallisation in each case<sup>149</sup> and in a related paper, L. R. G. Treloar<sup>150</sup> reports some experimental results which substantially verify the theoretical laws of photo-elasticity in the range in which crystallisation is absent. A qualitative indication is given of the variations of crystallisation which occur outside this range.

A survey of the factors affecting resilience has been made by R. E. Shaw,<sup>151</sup> in which comparisons are made between natural rubbers and neoprene compounds, the latter being regarded as superior in tensile, elongation, resilience, ageing, and oil-resistant properties, and the question of establishing energy losses due to hysteresis has been examined by S. Oberto and G. Palandri,<sup>152</sup> who draw attention to the importance of thermal conductivity and cooling conditions in this connection.

The importance of tear initiation and propagation has led to a number of experiments being carried out which demonstrate the existence of a maximum shear stress in sub-surface planes of the test sample and it is suggested that as the strength of the material is increased so the effects of the maximum shear stress are reduced.<sup>153</sup> The method used by the

Rubber Research Institute (Delft) for evaluating tear resistance has been examined and further experiments appear to indicate that at the moment of tearing an elongation is reached locally which is practically equal to the elongation at break of a standard tensile test. The conclusion is reached that the Delft method is to be preferred to the angle tear test.<sup>154</sup>

Among the factors influencing permanent set in rubber compounds, the most important appears to be the re-arrangement of the filler particles caused by stretching. The orientation of the filler can be accentuated by heat, resulting in an increase in the set, which, on the other hand, can be lowered by treatments involving the break-down of the filler structure.<sup>155</sup> The so-called permanent set is not really permanent and is not due to plastic flow except in badly under-vulcanised stocks. In an article dealing with permanent set, creep and recovery, S. D. Gehman<sup>156</sup> considers the influence of permanent set on creep in samples of *Hevea* and GR-S. At the initial stages of the creep test the flow appears to be largely due to the reversible yielding of relatively weak bonds which can reform under the action of the elastic net-work when the load is removed. For longer periods, however, or for higher elongations, the flow involves more deep-seated changes in structure. In further work on creep and relaxation, B. Gross<sup>157</sup> has presented a theory of the steady-state behaviour under alternating load and deformation and relations are established between the loss factor, the storage factor, the distribution functions and the Laplace transforms of the creep-and relaxation-function.

In the ageing and deterioration of rubber under exposure the influence of oxygen is, of course, paramount. The structure of the rubber molecule renders it susceptible to deterioration by molecular oxygen because the long molecules are broken into smaller units resulting in a degradation of physical properties. The influence of ozone, sunlight, and exposure to rain have been described by J. Crabtree,<sup>158</sup> who comments also on the effect of incorporating a light-absorbing filler, such as carbon black or ferric oxide, on the rubber compound. The action of sunlight and higher temperatures have also been discussed by G. Reinsmith,<sup>159</sup> who refers to the well-known discrepancies between natural ageing and artificial ageing tests and offers some suggestions on the interpretation of accelerated ageing test results. A method for measuring the oxygen-absorption of vulcanised rubber either in the dark or under illumination from a controlled light source has been developed,<sup>160</sup> and an article by R. Elliot and R. G. Newton<sup>161</sup> is concerned with the factors controlling the resistance to exposure-cracking when stretched rubber is exposed to outdoor atmosphere or to ozonised air.

The mechanical and optical characteristics of swollen rubber have been examined and an analysis given of the differences between the properties of swollen and solvent-free elastomers.<sup>162</sup> The stress-strain relation and the birefringence of rubber swollen in xylene-dibromoethane and a turpentine oil have also been investigated in relation to the statistical theory of swelling,<sup>163</sup> and the importance of the cohesive energy density of rubber and of the swelling liquid has been emphasised in a discussion on oil-resisting rubber published by the British Rubber Development Board.<sup>164</sup>

## Reclaim

In view of the extended use of synthetic rubber during and after the war, it is not surprising that the most significant developments in the field of regenerated rubber have been concerned with attempts to produce an improved synthetic rubber reclaim. Techniques applicable to natural rubber have not been found satisfactory and efforts have been directed mainly towards finding a catalyst for the reclaiming process which would prove more suitable with synthetics. A detailed investigation has been carried out<sup>165</sup> on certain polyalkyl phenol sulphides which, when used with the appropriate swelling agents and tackifiers, are claimed to give reclaims from GR-S and other elastomers at least comparable with those made from natural rubber, especially in regard to processability and physical properties. Test results also indicate that the polyalkyl phenol sulphide does not act by removing the sulphur from the vulcanisate and it is suggested that the reclaiming proceeds by the catalysing of the oxidative breakdown of the polymer with simultaneous inhibition of further cross linking reactions.

The trends in reclaim practice and the transition from a natural rubber base to materials containing both natural rubber and GR-S have been reviewed,<sup>166</sup> and comparisons made between present-day and pre-war reclaims. Although certain properties, such as the lack of building tack, inherent in GR-S, are reflected in the reclaim, it is claimed that many of the blends show distinct advantages. Processability is good, sticking to mill and calender rolls less pronounced and ageing characteristics have proved superior to those of pre-war material. As regards the present-day position, new grades of reclaim are available which are said to equal or surpass pre-war quality, especially as regards the important factor of uniformity.

The structure of polymers and its influence on behaviour during the reclaiming process have been investigated by D. S. Le Beau.<sup>167</sup> The changes in plasticity were measured when vulcanised GR-S and natural rubber were heated in steam at 200 lb./sq. in., and the author concludes that traces of oxygen probably play a part in the phenomena observed. The straightforward behaviour of natural rubber follows on the changes due to the reactive and methylene group, while the increased plasticity in the GR-S is followed by the formation of network structures through combination of active radicals and this leads to loss of plasticity and resulting hardness. The same author has also presented a series of studies on the basic reactions occurring during the reclaiming process,<sup>168,169</sup> and in dealing with the influence of reclaiming media, anti-oxidants, and defibre-ing agents on vulcanised natural rubber, has carried out an examination on molecular breakdown and the formation of oxidation products under varying acidic and alkaline reclaiming conditions. It is concluded that hydroperoxidic chain reactions are involved.

A few typical items on the production of reclaim selected from the patent literature may be included here. One method involves submitting the rubber, under high pressure and temperature, to the action of a mixture of saturated water vapour and the vapours of organic substances capable of making the rubber swell. The process is carried out at 180–210° c. for natural rubber and 200–240° c. for synthetic.<sup>170</sup> The cutting of

rubber into small grains (0.5 mm. minimum dimensions) before mixing with new rubber stock in proportions of up to 400% old rubber, has also been recommended,<sup>171</sup> and patents have been taken out for processes involving the use of thiophenol<sup>172</sup> and aryl selenide.<sup>173</sup> The electrostatic reclaiming of rubber by high-frequency fields can be carried out by placing the rubber between plates connected to a high frequency generator,<sup>174</sup> and a similar process involves heating finely divided rubber in a high frequency alternating electric field.<sup>175</sup> It is claimed that the temperature can be raised in this manner without harmful effect on the rubber.

### Adhesion and bonding

A general review of the application of adhesives in industry has been made by L. Puddefoot,<sup>176</sup> who defines an adhesive as a material capable of adhering at ordinary temperatures by means of "dry tack." The difference between "tack," cohesion, and adhesion is outlined and an alternative to the "Bostik" type of adhesive is suggested, using a primer and self-vulcanising cement.

German methods of bonding rubber to metal are the subject of two B.I.O.S. Interrogation Reports, in which the treatment of aluminium with alkali, nitric acid, and sodium zincate prior to brass plating is discussed. Comment is made on the use of Desmodur-R for stainless steel and cast-iron, for which brass-plating is not suitable, and on the application of a sub-layer of Buna-S before the Desmodur-R, which precludes a service temperature exceeding 80° C.<sup>177</sup> The best results in bondings using natural rubber were obtained with 20-30% zinc oxide, 2% sulphur, and a mercaptobenzthiazole-type accelerator. Brass-plating was considered to be the best process.<sup>178</sup>

The following is a necessarily brief selection made from the extensive number of patents covering processes for bonding rubbers to metals, glass, etc. Improved adhesion has been claimed in the brass-plating process by a prior heating of the metal with steam at over 290° F.<sup>179</sup> and bonding is said to be facilitated by the application of a high boiling long-chain fatty acid ester, such as *cyclohexanyl* stearate, to the freshly brass-plated metal.<sup>180</sup>

A cyclised product for bonding can be made by treating rubber with an alkali-metal alum, phosphorous pentoxide and sulphuric acid. This is heated in an atmosphere having an oxygen pressure less than normal air, at approximately 136-164° C. in the presence of 3% sulphur, selenium, or tellurium, and is claimed to give a bonding of 600 lb./sq in. adhesion.<sup>181</sup> According to another method rubber can be cyclised by the usual agents and then heat-bonded to metal, wood, or glass, using a cement prepared from partially hydrolysed polyvinyl acetate and a phenol-formaldehyde resin.<sup>182</sup>

A method of bonding laminates has been described using an adhesive, prepared from bituminous material emulsified with sodium metasilicate, which on the loss of water becomes "dilatent," i.e., undergoes a considerable increase in consistency upon the application of a sudden stress,<sup>183</sup> and the use of a composition based on natural rubber and a phenolic resin has been covered by two patents, one of which involves the addition

of a heat reactive oil-soluble phenol formaldehyde resin.<sup>184,185</sup> An aqueous solution of fluorosilicic acid or hydrofluoric acid in the presence of glass is recommended for bonding synthetic rubber to magnesium,<sup>186</sup> and a surface coating of rubber solution containing selenium dioxide or selenious acid has been used for applying to metal and glass before a layer of vulcanisable rubber is added and vulcanised in the usual way.<sup>187</sup> Magnesium and aluminium can also be treated with an acidified polyhydric alcohol such as ethylene glycol acidified by a strong mineral acid,<sup>188</sup> and the use of chlorinated polymeric materials and an organic polyisocyanate has also been recommended.<sup>189</sup> The use of a neoprene-resin compound as a one-application cement has been described,<sup>190</sup> and a review has also been given of developments in the application of phenolic and chlorinated rubber cements to die castings.<sup>191</sup>

Among the methods for bonding rubber to fibres and textiles the use of phenolic resins takes a prominent place. According to one process, an alkali-soluble resinous condensation product of a phenol and sulphur, when applied to the cords, is said to give an adhesion two and a half times that of the untreated cords,<sup>192</sup> and improvements in adhesion of up to 540% are claimed for the preparation of phenol-aldehyde resins and their incorporation into rubber; the use of ammonia or an organic amine is an essential part of this technique.<sup>193</sup>

The reaction product of an organic di-isocyanate and a natural or synthetic rubber (polychloroprene) in an inert solvent appears to be useful for bonding filaments to vulcanised elastomers,<sup>194</sup> and a process has been described by which fabrics are treated with a bonding metal, such as a suitable brass, which is deposited on the fabric to which the rubber is subsequently vulcanised.<sup>195</sup> Finally, mention should be made of two patents involving the use of resorcinol and formaldehyde. According to the first patent resorcinol and formaldehyde are added to a rubber latex<sup>196</sup>; the other patent describes the preparation of an adhesive comprising a co-polymer of butadiene or isoprene and alpha vinyl pyridine together with 10-90% by weight of heat convertible resorcinol-formaldehyde resin.<sup>197</sup> This is particularly recommended for bonding rayon or nylon to natural rubber or GR-S in the manufacture of tyres.

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# LEATHER AND GLUE

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## Collagen

X-RAY diffraction and electron microscope methods have been used in further studies on collagen fibre structure. Both methods show a giant repeating pattern along the fibre axis of about 640 Å. B. A. Wright<sup>1</sup> reports variations in the period from 628 Å. when the fibre is in an atmosphere of 2% R.H. up to 672 Å. at 100% R.H. Moisture uptake by the fibre was not uniform since there were changes in the intensities of the various orders of the diffraction pattern, the lower orders being most affected. This is also shown by E. F. Mellon,<sup>2</sup> who found that the amino groups of casein, 1% only by weight, are responsible for 25% of the total moisture uptake in the range 6–93% R.H. More moisture is taken up at the peptide links at the rate of 0.45–0.48 g. water per g. nitrogen in the main chain at 60% R.H. and this should be uniformly distributed. This figure applies to polyglycine, silk, and other proteins, but not to glycine polymers smaller than hexaglycine, *i.e.*, the larger polymers and proteins being imperfectly crystalline can take up water whilst the highly crystalline polymers cannot. Imperfect special packing of fibrous proteins is also mentioned below.<sup>5</sup>

Attempts to analyse the intensities of the interferences from low-angle X-rays have been made by O. Kratky.<sup>3</sup> The 642 Å. period may be divided into 220 periods each corresponding to one amino acid residue. Photometric curves of these periods show great variations in intensity and, on the assumption that the intensity is proportional to the molecular weight of the residue, it should be possible to allot specific amino acids to the more conspicuous spacings. No great accuracy is yet claimed for the attempt, nor was it possible since out of date figures for the chemical constitution of collagen were used.

The electron microscope shows light and dark bands along the collagen fibre. Those within the 640 Å. repeating period have been resolved by F. O. Schmitt and J. Gross<sup>4</sup> into five main bands. Two of these at higher resolution appear to be subdivided, making a total of seven dark bands, which may be due to the presence of atoms of high electron scattering power, or to greater thickness of protein, or to both. Moist fibres are of even thickness, but on drying, variations in thickness appear, giving the fibre a contoured outline. The dark bands retain their thickness whilst the light bands contract, showing that protein packing is denser in the dark bands. Similarly, on stretching the fibril develops a scalloped appearance the more intense bands retaining their thickness best. The lateral fine structure of the collagen fibril shows no recognisable repeating period larger than the inter-chain period of 10–15 Å., but longitudinal cleavage occurs under mechanical stress. The fibrils then appear to

be made up of filaments 50–100 Å. or less in width having axial bandings which are in register with those of the rest of the fibril. Tendon collagen shows the cleavage more readily than skin collagen suggesting that there the lateral bonding is weaker.

The fact that there is an orderly arrangement at distances as small as 100 Å. in collagen is considered by G. C. Nutting and R. Borasky<sup>5</sup> to preclude the existence of regions some of which are amorphous and others crystalline, rather suggesting that all the substance is crystalline but with imperfect spacial packing. However, amorphous regions may have been dispersed and lost during the preparation of the sample. The effect of various treatments on the banding has been studied.<sup>5</sup> Tannage and acid swelling both cause shrinkage in length of fibre. Collagens of low shrinkage temperature, such as shark skin corium and cowhide overlimed or soaked in saturated  $\text{BaCl}_2$  solution, show a marked deterioration in the regular fibril structure. The striations tend to disappear, but where they do appear the spacings are nearly normal. The swollen fibrils loop and twist. Hot water causes similar changes, the ends and outer surface of the fibrils dispersing first, the inner convoluted core finally dispersing. Elastin prepared from ligamentum nuchae was also examined. Only a reticular structure devoid of the fibrillation characteristic of collagen is shown. This finding that elastin, "though present as fibres in the ligament is reticular on smaller subdivision, makes more readily understandable W. T. Astbury's<sup>6</sup> observation that stretched elastin gives a diffraction pattern characteristic of an unoriented structureless material."

The reticular tissues (not necessarily reticulin) still present one of the most puzzling problems of protein fibre structure, possibly because if they are fine they are very difficult to identify and to isolate.

Striated muscle fibres are surrounded by a delicate membrane or sheath known as the sarcolemma. This has often been stated to be a network of fibrils, but W. M. Jones and R. Barer<sup>7</sup> can find no trace of fibrillar structure by microscopic means, including the use of phase contrast and dark-ground illumination, or by means of the electron microscope. The latter, however, revealed numerous spots about 0.04 to 0.1  $\mu$  diameter, approximately equidistant from one another and apparently on, not in, the membrane. It is suggested that these spots may be points of attachment of connective tissue fibrils or myofibrils, but the distance apart, 0.5  $\mu$ , does not coincide with any known periodicity of the myofibril. The spots are removed by treatment with dilute citric acid. Then, T. D. Day<sup>8,9,10</sup> has observed that whereas interstitial connective tissue forms a barrier to the passage of body fluids, when examined under the microscope it appears to be a relatively coarse network of fibrils which could not do so. Dark-ground illumination, however, reveals a continuous membrane of some lamellar "cementing substance" which invisible at  $p_{\text{H}}$  7, appears rapidly at  $p_{\text{H}}$  3.6, and then is seen to be composed of very fine angularly branching fibrils in which the smallest collagen and elastic fibrils are embedded like twigs on the surface of a frozen pond. Specialised sheaths of reticular tissue around relatively large collagen structures have been demonstrated before. This evidence suggests that smaller bundles owe their cohesion to the presence of an amorphous cementing

substance which causes a crimping effect on the bundles when they are swollen in acid solutions. This cementing substance—

is normally (*i.e.*, *ca.*  $p_H$  7) swollen, but becomes opaque slowly at  $p_H$  4.5, its apparent isoelectric point, and rapidly becomes opaque in more acid solutions;

is resistant to 0.001-N NaOH but is rapidly disintegrated by trypsin, a fact which may be significant in view of the loss of coherence and elasticity shown by connective tissue fibres on treatment with trypsin;

is not mucinous, being resistant to streptococcal hyaluronidase, testicular extract, and phosphate buffer  $p_H$  8.0.

A loss of coherence on digestion of another collagenous structure, cow or heifer hide corium, with trypsin has been found by K. H. Gustavson.<sup>11</sup> Hide pieces were prepared by washing with water and brine to remove inter-fibrillary proteins, and by splitting off the grain and flesh layers. Treatment of these pieces with water at 70° dissolved nitrogenous matter from them equivalent to about 10% collagen (from nitrogen estimation). Similar pieces after 24 hours in 0.1% and 1.0% trypsin solutions yielded 45% and nearly 100% collagen in water at 70° although the nitrogen content of the trypsin solution did not exceed 6% calculated as collagen. The trypsin treated hide showed only normal affinity for chrome tanning solutions, hence Gustavson concluded that the rupture of co-ordinate cross-links by trypsin had not occurred. But as solubilisation of the fibrous protein was probably caused by weakening of the cohesive forces within the fibres attributed largely to hydrogen bonds, the data presented do not suggest an explanation.

Solution of collagen by warm water is considerably aided by mechanical disintegration which forms an important part of a process for the production of collagenous strands such as surgical gut.<sup>12</sup> The prepared hide is swollen in dilute acid, *e.g.*, 0.1-N formic acid, disintegrated, and then passes into solution below 60°.

The effect of enzyme on the cohesion of collagenous structures, in this case damage to raw hides due to taint, is used by G. R. Volpert.<sup>13</sup> To assess the extent of the damage, single fibres are teased out from the hide, measured by microscopic methods, swollen in 0.13-N HCl and again measured. Normal-wet salted hide fibres show a contraction in length of about 45% due to the acid swelling, but the figure for tainted hide fibres is up to 62%. This he says is the result of removal of an envelope of inter-fibrillary protein which restricts swelling.

Different reagents may hydrolyse proteins in different ways. P. Boulanger and G. Biserte,<sup>14</sup> from studies of specific rotation of various protein fractions during hydrolysis, suggest that acid pepsin acts at several places along the molecule at the same time, whilst trypsin attacks the molecule bit by bit from the end.

Another new protein has been found by K. Bailey<sup>15</sup> in muscle fibrils. Tropomyosin appears to be a monomer molecule with the relatively low molecular weight of 90,000. A monomer which, having the ability of aggregating into fibres, is the unit utilised in the elaboration of myosin. There may be similar monomer molecules in other systems such as the keratins and collagens. A crystalline pre-collagen has apparently been

prepared by V. N. Orekhovich *et al.*<sup>16,17</sup> by extraction of finely ground hide, after removal of albumens and globulins, with citrate buffer at  $p_H$  4 and purification by dialysis. This pre-collagen is rapidly digested by cathepsin and papain and slowly digested by pepsin and trypsin. Ultra-violet absorption spectra of pre-collagen, albumin, globulin, and gelatin are mapped out. The globular proteins have also received attention from C. C. Kritzing,<sup>18</sup> who has reviewed their classification, and confirmed details of their distribution in the hide and methods of extraction. The grain area of hide contains a higher proportion of globular proteins than the corium. Furthermore, a few days' soaking of fresh hide in a 10% NaCl solution causes hair loosening and there seems to be some relationship between hair loosening and amount of nitrogenous matter removed.

### Keratin

There are differences between the proteins of cuticle, cortex, and medulla. J. L. Stoves<sup>19</sup> points out that caustic alkalis dissolve the cortex leaving the medulla behind, which then contains far less sulphur than the cortex keratin. (Perhaps some sulphur has been removed by the alkali as S. Blackburn<sup>20</sup> finds only a slight reduction.) But the cortex is not attacked by trypsin whereas if the medulla is exposed, as in a section, it is rapidly attacked by trypsin. Blackburn<sup>20</sup> found that medulla from some sources is composed largely of amino acids without active side chains and is in the  $\beta$ -form (fully extended molecules) whereas the cortex, with more active side chains, is in the  $\alpha$ -form. He therefore suggests that some of the differences in reactivity are due to differences in compactness of structure. It is worth noting that some of the sulphur present in keratin was not identifiable as cystine, methionine, or lanthionine sulphur. Another complication is the finding by J. Lindberg *et al.*<sup>21</sup> of a thin protective membrane covering wool fibre. This is only 0.1% of the wool by weight but is not dissolved by sodium sulphide solution. Under the electron microscope it appears to have a thickness of 50–100 Å.

### Vegetable tannage and tanning materials

A review of the factors controlling the vegetable tanning process has been given by M. P. Balfe.<sup>22</sup> These factors operate mainly through their effects on the swelling of the hide protein. The account includes methods of estimation of the acids and salts contents of tanning liquors and extracts and of their effects on the tanning process.

Criteria of tannage used by P. Chambard<sup>23</sup> are (i) the measurement of resistance to hydrolysis and (ii) of the dehydration produced by the tannage. Resistance to hydrolysis is taken by him to be related to the shrinkage temperature as measured in a bath having a  $p_H$  value similar to that of the sample, but certain alum tanned leathers have a low resistance to hydrolysis and a high S.T.; consequently, the Fahrion method is used instead. This involves determination of the amount of hide substance passing into solution on boiling in water for 10 hours.

An extensive review of the many theories of vegetable tannage has been given by S. G. Shuttleworth and G. E. Cunningham.<sup>24</sup> After discussing

the hydrogen bond theory they conclude that it adequately explains all the known facts.

The shrinkage temperature is commonly taken as an indication of the strength of the lateral cohesion in the molecular structure of the leather (or pelt) and the increase normally caused by tannage is attributed to the formation of additional cross-links in the protein structure by the tanning agent. J. H. Highberger<sup>25</sup> had assumed that an increase in S.T. should therefore result in an increase in mechanical strength, but produces evidence that this is not true. He found that individual fibres have a tensile strength of 10–12 kg./mm.<sup>2</sup> Vegetable tannage halved this figure, and formaldehyde tannage reduced it still more. That is, the tensile strength falls as the S.T. rises. Highberger concludes, therefore, that the cross-linkage theory of tannage needs revision. Shuttleworth and Cunningham<sup>24</sup> have criticised this conclusion for the reason that tensile strength depends considerably on the degree of longitudinal slip of the molecular structure. This permits readjustment of fibrils and of molecules so that the strain is more evenly distributed. Cross-linking between individual chain molecules might be expected to restrict molecular slip and so reduce the tensile strength of the fibre. This criticism seems justifiable.

Gelatin strips, in which there is little molecular orientation, show no shrinkage in hot water as they stretch near melting point. Schweikert<sup>26</sup> confirms Chater's<sup>27</sup> observation that when tanned with alum or vegetable tannins they behave in the same way, but the temperature at which stretching begins varies. Chrome and formaldehyde tannages however do produce a strip which shrinks in water at 45–50°. These observations are taken as evidence of cross-link formation by chrome and formaldehyde and failure to do so by vegetable tannins.

The precise nature of the link or links between the vegetable tannins and collagen has been, and is likely to be, the source of much speculation. This year's contribution does little to clear up the confusion. Shuttleworth and Cunningham<sup>24</sup> dismiss all but the hydrogen bond. S. S. Kremen and R. M. Lollar,<sup>28</sup> from studies of the tannage of calf skin and deaminised calf skin at various  $p_H$  values, find no evidence of salt formation with quebracho and myrabolam, but some evidence of salt formation with two different ligno-sulphonates. The latter are remarkable for their resistance to alkaline stripping. H. B. Merrill *et al.*,<sup>29</sup> after studying the stripping effect on vegetable tanned leathers of various organic solvents with or without added water, conclude that tannin combines chemically with collagen, the increase in stripping power on adding organic solvents to water being due to repression of ionisation or reduction in the molecular weight of the tannin. K. H. Gustavson,<sup>30,31</sup> on the whole, supports the salt formation theory, but some of his conclusions seem questionable. Calf pelt or hide powder is tanned with vegetable tannins or ligno-sulphonic acid, washed thoroughly, and dried. Weights of material, equivalent to 1 g. of dry collagen, are then immersed in 25 ml. 0.1-N HCl containing 0.4 g. NaCl and after reaching equilibrium the external solution is titrated using methyl red indicator. The figures for fixed HCl, obtained by difference, are given in the table. The vegetable tanned collagen, although its HCl fixing capacity is nearly that of raw

collagen, if retanned with ligno-sulphonic acid fixed only about one-third of the quantity fixed by raw collagen. It is therefore concluded that the modes of combination must be different. This would be so if the collagen amino group was responsible for both HCl and tannin fixation, but acid fixation in the range 5 to 2  $p_H$  is due to repression of ionisation of the carboxyl group, and, as far as is known, is not affected by the amino group. The differences found seem to be due to the  $p_H$  of the collagen when immersed in the HCl solution. This  $p_H$  would be expected to vary with the  $p_H$  of the previous treatment and the amount of washing given. The  $p_H$  of the final tanning solutions are also given in the table. Any other conclusions based on the HCl fixing ability of the tanned collagen seem to be of little value.

Tannage	HCl fixed ml. per g. collagen	$p_H$ of final tanning solution
None .. .. .	0.94	—
Quebracho .. ..	0.88	5.5
Mimosa .. .. .	0.88	4.8
Myrabolan .. ..	0.78	3.2
Ligno-sulphonic acid ..	0.04	1.3

The chemistry of the natural vegetable tannins has received further attention. G. N. Catravas and K. S. Kirby<sup>32</sup> have separated sumac tannins into several fractions by precipitation with varying amounts of aluminium hydroxide. The main fractions were then methylated and purified further by chromatographic adsorption on alumina from benzene solution and elution with benzene-ethanol solvent. The results of examination of these fractions indicate that the tannin is mainly a mixture of *m*-digalloyl-trigalloyl glucose and di-(*m*-digalloyl)-galloyl glucose.

They have also examined the acetone soluble fraction, 66%, of mimosa tannin fractionated by chromatographic adsorption with alumina. Results of the examination of these fractions suggest that the union between catechin units in the build-up of tannin depends on opening up the oxygen ring as suggested by Freudenberg, but linking up with the pyrogallol nucleus, not with the resorcinol nucleus. Furthermore, the number of units in the molecule is estimated to be five from the number of end groups left free (m.wt. 1500). This formula covers two fractions, one having a pyrogallol nucleus and the other a catechol nucleus for the link up.

S. G. Shuttleworth<sup>33</sup> has also disagreed with Freudenberg and considers the build-up from the catechin unit to be due to hydrogen bond formation: He argues that the red colour developing on exposure to light or acid indicates change of the resorcinol ring to the keto form, which is suitable for the hydrogen bond linkage.

Aqueous spruce bark extract has been separated into three fractions by A. Kuntzel and E. Melzer.<sup>34</sup> One of these, (a), is insoluble in 85% ethanol, will not penetrate pelt, and gives negative tests with reagents for tannin, so it cannot produce leather. The other two fractions, both soluble in 85% alcohol, and one of them, (c), soluble also in absolute alcohol, are capable of producing good leather. Fraction, (c), is also rich in phenolic non-tans which have a useful function in the tanning

processes. These non-tans are important from the analytical point of view since they are not precipitated by lead acetate and reduce Fehling's solution. The normal method of estimation of sugars, therefore, can give very inaccurate results. Sulphiting spruce bark extract is shown to reduce the proportion of fraction (c), but increases the proportion of fraction (a), which will not tan.

World anxiety over the shortage of vegetable tanning materials is reflected in the number of papers reporting investigations into the properties of, and optimum conditions for the extraction of, tan from less well known materials, *e.g.*, Canaigre,<sup>35</sup> Konnan bark,<sup>36</sup> Sumac,<sup>37</sup> and oak slabs.<sup>38</sup> The oak slabs left by saw mills in Tennessee Valley, U.S.A., have been a nuisance except when required as fuel, but they contain about 4% tan of good quality and it can be extracted at reasonable cost. On average, they consist of 40% bark and 60% wood. The spent chips, after removal of bark, can be pulped with sodium sulphite to give excellent corrugated paper. They can also be hydrolysed by acid to yield 42% sugars (on dry weight basis), suitable either for the production of alcohol or as nutrient for a high protein yeast, and furfural.

Leaching efficiency in the preparation of tanning extracts has been investigated by S. S. Sourlangas,<sup>39</sup> who demonstrates losses of 16½% of the original tan and 5% of the soluble non-tans due to destruction or precipitation.

### Sulphite cellulose and synthetic tanning materials

Fractionation of sulphite cellulose liquors by dialysis into four fractions has been effected by F. M. Erusberger and W. G. France<sup>40</sup> and their properties examined. The poorest fraction consisted almost exclusively of sugars and salts and was rejected. Results of examination of the others were:

	Average molecular weight	Sugars % of total solids	Equivalent weight	[H]/S
1.	9500	0	519	1
2.	2140	2.6	316	1.37
3.	250-940	31.0	249	1.84

They take the equivalent weight figures as evidence of a higher degree of sulphonation in fraction 3, but suggest that the high ratio of hydrogen ions to sulphur indicates the presence of carboxyl groups.

It is also shown that ligno-sulphonic acids and their salts in aqueous solution are only 20-60% dissociated, a fact offered as explanation of their behaviour as cation exchange resins.

Purification of sulphite cellulose liquors by dialysis and analysis by Q. P. Peniston and J. L. McCarthy<sup>41</sup> has resulted in the suggestion that there may be some sulphonic acid derivatives of sugars present since purification alters the ratio of methoxy groups to sulphur. There appear to be no hydroxyl groups in the molecule of ligno-sulphonate though mild alkaline hydrolysis produces some, and also chlorination followed by alkaline hydrolysis.<sup>42</sup> Hydroxyl groups in the tannin molecule have important properties. This is again shown by G. I. Kutyanin.<sup>43</sup> Tannin fixation by hide powder from solutions of quebracho or resorcinol/formaldehyde liquors is excellent, and bound water-solubles also are

high. These materials have no sulphonic groups but numerous hydroxyl groups. Tannin fixation is moderately good but bound water-solubles poor from sulphite cellulose which has sulphonic groups but few hydroxyl groups. Tannin and bound water-solubles figures are poor from condensed naphthalene and naphthol sulphonic acids which again are deficient in hydroxyl groups. Confirmation of the value of polyhydroxy-tans is given by J. H. Highberger *et al.*<sup>44</sup> who found the best results from the resorcinol-furfural products. These, blended with sulphite cellulose waste liquors are stated to produce leathers comparable with those from an American tannery using normal vegetable tanning materials.

There are reports of a new synthetic tan, suitable for sole leather production, developed by Winheim and Doherty.<sup>45</sup> A di-aldehyde is first reacted with the hide, then built up *in situ* into a full tannage by urea, phenol or resorcinol and formaldehyde. The reaction between glyoxal or methylglyoxal and the basic groups of collagen has been described by K. H. Gustavson,<sup>46</sup> whilst another synthetic tannage, also involving the basic groups of the collagen, has been investigated by J. B. Brown *et al.*<sup>47</sup> This is a sulphonyl chloride and is most suited for clothing leathers. The outstanding features of the leather are high tensile strength and pliability at very low temperatures.

### Mineral tannage

A detailed study of the rate of absorption of chromium during drum tannage has been made by P. S. Briggs<sup>48</sup> for semi-chrome leathers. There is an abnormally large uptake of chrome during the first five minutes' contact, after which the rate of reduction of the chrome concentration of the liquor conforms to a mathematical equation. The constants in this equation change with the basicity of the liquor, the initial concentration of chrome, the effectiveness of masking agents, etc. The "contact drop," and the rate of chrome uptake immediately following it, are greater when the liquor is more basic, but after a time in all cases the rate of exhaustion of the liquor becomes very slow unless the basicity is again increased. The ideal curve would be less steep in the early stages and steeper in the later stages (obtainable by trickle-feed of alkali).

The final  $p_H$  of the alkali stripping bath before chrome tannage, in spite of thorough washing between processes, had a profound effect on the rate of chrome uptake. Similarly, C. C. Kritzing and E. R. Theis,<sup>49</sup> working with full chrome tannage, found that the previous process, in this case pickling, had a considerable effect on the distribution of chromium between grain, corium, and flesh layers. Too weak or too short pickling leaves alkali in the middle of the pelt in sufficient quantity to produce some case-hardening, whilst too strong a pickle puts acid in the middle, so that chrome fixation is retarded and, again, there is too little fixed chrome in the middle. The figures demonstrating this were obtained by splitting the leathers into ten layers of approximately equal thickness for separate analysis. Liquors of too high basicity tend to tan the outer layers too heavily but masking the liquor usually tends to level this out. Formate masking was found to be most effective, but phthalate masking tended to exaggerate uneven fixation so that phthalates should be more useful as neutralising agents. However, these conclusions as to the

effectiveness a masking agents may not be very reliable as the sodium salts of the acids were used, often in high concentration, without control of  $p_H$ . In another paper E. J. Serfass and E. R. Theis<sup>50</sup> are forced to use the free acids owing to precipitation of chrome by the salts.

Evidence of the penetration of acid anions into the cationic chrome complex, and of the formation of anionic chrome complexes, is now considerable. D. A. Plant<sup>51</sup> used three methods of showing changes in complex formation due to addition of various salts to chrome alum solutions: (1) ionic sulphate estimation by benzidine precipitation, (2) free organic acid estimation by ethyl acetate extraction, and (3) by spectrophotometric curves which, from increase in optical density at selected wavelengths, give a measure of complex formation. Phthalate was found to penetrate very rapidly into the complex of fresh chrome alum solutions but very slowly when the solutions were aged and sulphate ions had to be displaced from an already formed complex. The tendency for organic acids to enter the complex becomes smaller as the dissociation constant of the acid falls because it is the acid anion concentration which is effective and at prevailing  $p_H$  values this decreases rapidly as the  $p_K$  value rises. Electrophoretic results showed that the chrome in chrome-tanning powder and strong boiled solutions (10%) of chrome alum was mainly anionic, whilst in less concentrated boiled chrome alum solutions it was both anionic and cationic in proportion depending on the concentration.

The spectrophotometric method was also used by E. J. Serfass and E. R. Theis,<sup>50</sup> who assumed that the hyperchrome effects measured were proportional to the ease of penetration of the added organic acids into the chrome complex. This was in the order oxalate > citrate > tartrate > acetate > formate > sulphate.

A similar order was found by E. R. Theis *et al.*<sup>52</sup> using the cation exchange resin. (They also assessed the particle size from diffusion experiments.) The chrome liquor was left in contact with the resin for 20 minutes, filtered off, rinsed, and the retained chrome was extracted by 6-N sulphuric acid solution. The two solutions were analysed to determine the distribution of chromium, sulphate, and organic acid anions. This work has been criticised by J. D. Tolliday *et al.*<sup>53</sup> who state that at some of the concentrations employed the efficiency of the resin must have been very low. Further doubts as to the validity of the results are raised by the observation of Serfass and Theis<sup>50</sup> (quoted above) that the sodium salts of weak acids, as used in these experiments, caused precipitation of chromium in some cases.

More studies of the conductimetric titration curves of basic chrome sulphate solutions at extreme dilution have been reported by S. G. Shuttleworth.<sup>54</sup> After comparing the effects of adding various monobasic acids and their salts and gelatin he concluded that in chrome tannage, the sulphate groups of the chrome complex are replaced by the carboxyl groups of the protein. This takes place more rapidly as the basicity of the chrome-liquor increases. Apparently the amino groups of the protein do not enter the complex during the tannage but may do so during drying. Masking agents in the acid form do not de-olate the chrome complex appreciably. Complexes are formed (in order of decreasing

stability) with salicylaldehyde > pyrogallol > catechol, but none are formed with phenol, resorcinol, hydroquinone, phloroglucinol. The conclusion that "for complex formation it would seem to be necessary to have oxygen atoms placed in suitable positions for ring formation to occur" conforms to the theory reviewed by Plant<sup>51</sup> in the early part of his paper. It is also suggested that in semi-chrome tannage the tendency for the vegetable tannins to form complexes with the basic chrome-liquors should vary with the type of tannin, quebracho forming the least stable, and tannins containing organic acid groups the most stable complexes. The latter should be capable of some de-chroming when applied after the chrome tannage.

It has been shown by I. P. Strakhov<sup>55</sup> that cationic chrome is fixed from the usual one-bath tannage, but anionic chrome is fixed by the two-bath tannage. Normal solutions of Rochelle salt and oxalic acid strip less chrome from leather tanned by the two-bath method than from leather from the one-bath tannage, but the figures are reversed when stripping with 0.5-N NaOH. This is taken as evidence that fixed chrome is anionic from the two-bath tannage and cationic from one-bath tannage. Confirmation is obtained by tanning leathers with one- and two-bath processes and with anionic chrome liquors and comparing the results. Similar results were obtained from the two-bath and anionic chrome tannages from which sodium hydroxide stripped one-third of the chrome compared with about 8% stripped from the one-bath (cationic) tannage. Oxalic acid and Rochelle salts strippings removed less chrome from the anionic tannages than from the cationic.

More information on the composition of the fixed chrome-complex in leather is given by L. Seligsberger<sup>56</sup> from estimation of the acid anions present. Formate and acetate are removable from the leather by hot water, whilst others, *e.g.*, sulphate, phthalate, oxalate, are more firmly held. Ammonia can displace 95% of the sulphate and the organic anions. (Methods of estimation are given.) The results show that fixation of organic acids by the leather does not increase proportionally with their concentration in the liquors. It is, therefore, deduced that additions of more than 0.33 equivalents of organic acid anions per gram-atom chrome become wasteful. During drying of chrome leather, much formate is lost, but sulphate and phthalate are not. This is tentatively suggested as the explanation of tannery experience that formate masking tends to produce a flat, spready leather whilst phthalate masking gives a full leather of lower area.

Zirconium salts are in some respects similar to chrome salts and give a white tannage. Details are given by I. C. Somerville and H. G. Turley.<sup>57</sup>

## Mycology

There has been a review by A. J. Musgrave<sup>58</sup> of the activities of moulds and yeasts as they affect the leather industry, followed by a list of fungicides from J. N. Turner *et al.*<sup>59</sup> which has been abbreviated to a short list of 15 "accepted leather fungicides." This information is very useful for reference purposes. A more specific treatment of the problem is given by Kanagy *et al.*<sup>60</sup> who evolved a formula for a fungicidal leather dressing for use in the tropics. This dressing includes oil to maintain pliability

in the leather, a solvent for oil and fungicide, and two fungicides. Tests were carried out on the treated leather after extensive soaking in water so that there was little risk of choosing a fungicide which would fail in a wet climate. Mustiness in shoes is also due to moulds and has been the subject of work by A. Colin-Russ.<sup>61</sup>

Tests of fungicides applied to shoe linings described by L. C. Barail<sup>62</sup> include measurements of their tendency to cause irritation. This is done by means of injection and patch tests on mice.

### Analysis and testing

Estimation of the nitrogen content of organic materials is still the cause of much trouble, some of which arises from attempts to shorten the time. The potassium sulphate-copper sulphate catalyst is slow and an extension of the digestion time, to at least twice the time required to clear the mixture, is required if the full nitrogen content is to be converted to ammonium salt. Even then some organic ring compounds are not completely digested. However, extension of the time of boiling does not cause loss of nitrogen. Digestion time is considerably curtailed by using selenium as a catalyst, but undue extension of the time of boiling leads to low results. Use of a mixture of selenium and mercuric oxide is as quick, and gives less loss of nitrogen through over-boiling. Both these selenium catalysts are far more effective on organic ring compounds than copper sulphate. These points are clearly shown by experimental results of S. M. Patel and A. Sreenivasan.<sup>63</sup> The selenium catalyst is not to be recommended for general purposes though it has its uses. R. E. Seebold<sup>64</sup> has come to the same conclusion.

In leather analysis one of the difficulties of the Kjeldahl method is that as the leather itself is not homogeneous a relatively large sample, *viz.*, 1.5 g. is needed and the shavings or cubes of material must contain the proper proportion of grain, middle, and flesh. Digestion of this large quantity requires longer than with small quantities. A. Harvey<sup>65</sup> has, however, obtained good results from a semi-micro method using 0.1 g. of very finely divided leather sample, copper sulphate catalyst and steam distillation of the ammonia into boric acid for direct titration using a screened indicator. Digestion time is 10-15 minutes to clear, plus 10 min. over-boil. Other methods designed to save time include digestion with hydrogen peroxide followed by iodometric determination<sup>66</sup> or the formaldehyde titration<sup>67</sup> and absorption of the ammonia by diffusion<sup>68</sup> instead of distillation.

The factor converting nitrogen into hide substance has been criticised by J. H. Bowes and R. H. Kenten.<sup>69</sup> Their analysis of hide collagen has shown an average nitrogen content of 18.1% and of sheep skin, an average of 17.2% whereas the accepted figure is 17.7%.

Another very common determination, that of moisture in leather, has received attention. J. R. Kanagy and A. M. Charles<sup>70</sup> using a forced draught oven, show that equilibrium is reached in 4 to 6 hours' drying at 80° for all the leathers examined. The figure so obtained is therefore at least a reliable reference figure, whereas at higher temperatures prolonged drying gives a continual loss of weight and the result depends on both time and temperature.

The use of cation exchange resins for analytical purposes has developed during the past few years. J. D. Tolliday<sup>63</sup> *et al.* have examined the efficiency and methods of use of modern exchange resins and show that efficiency depends on (1) the nature of the cation, divalent calcium being more readily adsorbed than sodium, (2) on the  $p_H$  of the solution since low  $p_H$  values reduce adsorption of cation, and (3) on the nature and concentration of the anions which tend to be adsorbed by the resin if time of contact is long. The best results are obtained using the percolation method with cation concentration below 0.003-N and a short time of contact. Ion exchange resins have been used for the separation of acidic amino acids<sup>71</sup> and basic amino acids.<sup>72</sup>

Analysis of sulphite cellulose materials is not satisfactory by the normal official methods using detannisation by means of hide powder, but J. R. Salvesen<sup>73</sup> now states that complete de-tanning takes place at 45° in the normal time. He suggests that it is fair to use the same conditions, *viz.*, complete exhaustion, for all types of tanning materials.

The normal method of estimating the sugars present in tanning liquors, reduction of Fehling's solution after precipitation of tans by lead acetate, has been shown to be unreliable.<sup>34</sup> (See above.)

Estimation of chromium contents of chrome-liquors can be simplified. S. Wolstenholme<sup>74</sup> recommends oxidation using perchloric acid followed by direct titration with ferrous sulphate using *N*-phenylanthranilic acid. By this method, removal of the iron before titration is unnecessary. Sodium peroxide oxidation will not suffice as it fails to destroy organic hydroxy-acids (if present) which interfere with the titration.

The rate at which water enters vegetable tanned sole leather immersed in it is, rather surprisingly, independent of the temperature after the first few minutes and is not affected by the addition of wetting agents. This is shown by R. H. Hall and R. G. Mitton.<sup>75</sup> For the first period of perhaps 15 minutes the water enters very rapidly through the capillary spaces in the leather, delayed at times by trapped air bubbles, then swelling of the fibres narrows the capillaries so that further entry becomes slow and may finally depend on diffusion of the water through the solid material of the leather. Wetting agents hasten swelling of the fibres.

Water penetration of upper leathers under dynamic conditions has been investigated by C. E. Weir *et al.*<sup>76</sup> Their apparatus flexes the leather sample until water placed on the upper side penetrates to congo red paper fastened to the lower side. All commercial leathers tested showed a low resistance to wetting under these conditions. Water penetrates more rapidly from the grain side although the grain layer offers the principal barrier to water penetration. This is attributed to a pumping action caused by filling of hair follicles whilst the leather is flat followed by closing of the entry and squeezing as the leather is bent grain inwards. Greasing the leather is not a reliable way of increasing resistance to water penetration, presumably as capillary space is seldom completely blocked. A hard dubbin, for example, may form cracks during flexing of the leather. It is shown by W. J. Roddy and D. B. Gapuz<sup>77</sup> that stuffing increases the resistance of leather to water more than fat-liquoring although the composition of the stuffing mixture is not important.

Examination of a large number of American Army shoes by the Maeser

walking machine and by actual wear tests has been shown by W. J. Roddy<sup>78</sup> to give similar results for water penetration. The shoes became very wet in five minutes when walking in three inches' depth of water, and it was clear that the leather used was not made to withstand such conditions.

A number of worn Army boots have been examined by L. M. Whitmore *et al.*<sup>79</sup> to find the cause of deterioration of insoles and welts. The data suggest that deterioration starts with the action of perspiration and water which, aided by the blotting action of socks, raise the  $p_H$  of the leather, remove oil and water soluble matter and initiate corrosion of iron fastenings. Further deterioration is accelerated by the resulting iron contamination.

Physical test results of leathers are complicated by the variability of samples taken from different locations in the same hide or skin. R. G. Mitton,<sup>80</sup> after careful examination of variability of calf skins, has recommended that for tensile-strength tests, the skins should be sampled in the butt area and the pull should be across the run of the fibres (hair follicles). This gives the lowest but least variable results.

Machinery used for physical tests and automatic recording of the results has been discussed by R. B. Finch.<sup>81</sup> His work is with textiles, not leather, but some of the problems are similar. Amongst the devices used are a servo-mechanism to ensure constant rate of extension, and a strain gauge for measuring change of tension whilst examining tensile properties.

The accelerated ageing tests of Kanagy, officially described as a test of deterioration at high temperature, has been criticised by Shu-Tung Tu.<sup>82</sup> The test involves seven days' exposure at 100° and 10% R.H. and is shown to give vastly different results from those of five years' storage of chrome-iron and chrome- and iron-tanned leathers. The objection raised is to the high temperature of the test.

### Miscellaneous

Tannery waste treatment is described by H. T. Reuning,<sup>83</sup> who recommends screening to remove hair, fleshings, string, etc., which would interfere with free flowing of the sludge; collection of all wastes in a tank large enough to hold the effluent flow expected during one hour and mechanical mixing there; followed by sedimentation in a tank of at least six hours' capacity. This should remove almost all suspended solids and 90% of the B.O.D. if there is no vegetable tan present but only 80-90% of suspended solids and 50% of the B.O.D. when vegetable tan is present. Further purification can then be effected by filtration, chemical coagulation and re-filtration.

Large numbers of bacteria have been found in artificial bate liquors and identified by E. C. Line.<sup>84</sup> Most are proteolytic. Micro-organisms also play a large part in the raw hide or skin. F. L. Jones,<sup>85</sup> in describing the more important physical properties required in chrome-calf leathers concluded that they are very much dependent on the condition of the raw stock since a poor cure results in patches of skin which change more rapidly during liming and so tend to give loose grained leather with bad vein marks. Other points are mentioned such as the need for thorough removal of degraded keratin from the grain before tannage and the use

of a sufficient concentration of neutral salts in the tanning liquor to check pelt swelling, which would give a low grain strength. The importance of post-mortem changes in the hide or skin is also stressed by M. Dempsey.<sup>86</sup> The epidermis is an efficient barrier to the penetration of bacteria, but they can penetrate from the flesh side, principally through blood vessels and veins, and may reach the grain within three days. A method of assessing the amount of deterioration due to taint has already been described above.<sup>13</sup>

Sole leathers are frequently treated with Epsom salts and sugars after tannage. J. H. Bowes<sup>87</sup> describes experiments showing that the action of the Epsom salts is mainly that of salting out the excess tan. There is also a fall in  $p_H$ , for example, a mimosa liquor at 100° B.  $p_H$  3.24, on mixing with an equal volume of saturated Epsom salts solution, dropped to 2.8  $p_H$ . Little magnesium tannate was found below  $p_H$  4, however. The ease of salting out varies with the tanning material. The function of the sugars often added is to aid penetration of the salts by restraining precipitation and to reduce the tendency for spue formation. J. H. Bowes<sup>88</sup> *et al.* also show that the Epsom salts treatment not only improves the colour of the leather, but also reduces the tendency to crackiness when the leathers are very dry.

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# INSECTICIDES

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FOR this report certain topics have been selected from amongst the great number available. The topics selected appear either to be applications of general interest or work of fundamental importance.

## Systemic and other phosphorus insecticides

Several insecticides, the main uses of which are considered to lie in their property of facile dissemination throughout the tissues of a plant, were described in the last annual report by J. T. Martin.<sup>1</sup> The great drawback to most of such compounds, which are usually phosphoryl esters and reactive fluorine derivatives, is their high toxicity to warm-blooded animals.

The most active constituent of the non-systemic mixed phosphoryl esters, originally formulated as hexaethyl tetraphosphate, is tetraethyl pyrophosphate. This compound, which can be obtained pure by repeated distillation, is about seven times as toxic as the crude mixed esters, and has been shown to be a powerful depressor of cholinesterase in warm-blooded animals and insects.<sup>2</sup>

It was found that the hydrolysis of tetraethyl pyrophosphate in water is a first-order reaction with half-life of 7 hours at normal temperature, and 4 hours at 36.5°. No alcohol is formed on either alkaline or acid hydrolysis, and it is inferred that the pyrophosphate yields diethyl orthophosphoric acid.<sup>3</sup>

The  $Q_{10}$  for the rate of hydrolysis is 1.7 at constant  $p_H$ , when the half-life is 324 min. at  $p_H$  7 and 25°.

Blocking of the cholinesterase systems<sup>4</sup> is also held to be responsible for the toxicity of E.605 ("Parathion") or diethyl *p*-nitro-phenylthiophosphate. The hydrolysis of "E.605" in saturated solution in water at 20–25° (20 p.p.m.) has a half-life of 120 days.<sup>5</sup> In the presence of saturated lime-water this value is reduced to 8 hours. These reactions are also first order with respect to both ester and hydroxyl ion.

A committee of the U.S.D.A.<sup>6</sup> under Dr. P. A. Neal, has formulated precautions for the use of phosphoryl ester insecticides, which are reported to have about the same toxicity as nicotine. Atropine is the only satisfactory antidote, but should be administered under medical supervision.<sup>7</sup>

A simple, rapid, and reliable method for the determination of phosphoryl ester insecticides is given by Jacobson and Hall. Alkali-nitrate fusion, and dilute nitric acid digestion, is followed by colorimetric determination of the yellow molybdo-phospho-vanadic acid formed in the usual way.<sup>8</sup>

Probably the most important current use of phosphoryl ester insecticides is to control hemipterous (sucking) insects such as greenfly, and for this purpose the properties of the newer insecticides are somewhat similar to those of the well-established remedy, nicotine. Dusts, for example,

containing 0.5% diethyl *p*-nitrophenylthiophosphate ("E.605" or "Parathion") have given excellent control of the very widespread aphid *Myzus persicae*.<sup>9</sup> This insect is one of the most important carriers of numerous virus diseases.

### Vegetable insecticides

Apart from pyrethrum preparations, which are the subject of a good deal of active research, relatively little work has been published on the older insecticides of vegetable origin. Nicotine maintains its use for the control of aphids on green vegetable crops. Under favourable conditions, control may be achieved by fumigation with nicotine under tarpaulins drawn by tractors over the rows of, say, a brassica crop. Competition in this type of pest control is already being experienced from the phosphoryl ester insecticides, which, however, are just as dangerous to handle as nicotine, if not more so.

Relatively few papers of chemical interest have appeared on other insecticides, the active principles of which are alkaloids. The interest shown in *sabadilla* dust, the ground seeds of *Schoenocaulon officinale* seems not to have been maintained, but "Ryanex," or powdered *Ryania speciosa* gives protection against the sugar cane borer,<sup>10</sup> and the extracted roots of *Heliopsis longipes* have been found<sup>11</sup> toxic to houseflies. E. J. Seiferle and D. E. H. Frear<sup>12</sup> have reviewed the literature of plant insecticides in general, and the less common plants having ingredients of possible utility as insecticides have been listed and discussed by R. C. Rourk.<sup>13</sup>

### Pyrethrum synergists

Synergism in insecticidal preparations has received considerable attention in the past few years. Its definition, which tends to vary from author to author, has been discussed by D. J. Finney,<sup>14</sup> and usually implies that a synergistic mixture of insecticides is one for which the actual toxicity is greater than that expected by summing the toxicities of the constituents. The opposite effect is that of antagonism.

Pyrethrum preparations in particular can be synergised by several compounds, a notable recent addition to the list being piperonyl butoxide.<sup>15</sup> This compound was evolved as a successor to piperonyl cyclohexanone, the synergistic effects of which were studied by Piquett, Nelson, and McGovran,<sup>16</sup> and much attention has been given to compounds containing the methylene dioxy-grouping by Synerholm. Substances of the type represented by  $\alpha$ -phenyl-(3:4-dioxymethylene)-acrylonitrile,<sup>17</sup> and various partially hydrogenated dioxymethylene methyl naphthalene dicarboxylic acids<sup>18</sup> have been described. La Forge,<sup>19</sup> has prepared 2-(3:4-dioxypheyl)-tetrahydropyran, and Wacks<sup>20</sup> has recommended the use of diethylene glycol-4:5-methylene dioxy-2-propyl benzyl butyl ether. These compounds, like piperine<sup>21</sup> itself, are doubtless intended to act in the same way as sesamin, which is a well-established synergist for pyrethrum preparations containing two methylene dioxy phenyl groups on a condensed tetrahydrofuran residue.

Piperonyl cyclohexanone and piperonyl butoxide are also stated to be synergists for rotenone, the active principle of derris.<sup>22</sup>

Similar compounds for which claims have been made of synergistic action with the pyrethrins are the cyclic acetals containing the 3:4-methylene dioxypheyl radical.<sup>23</sup> Jones and Bushnell<sup>24</sup> claim that dialkyl phthalates are synergists for the pyrethrins, but this claim seems improbable in view of the fact that most of the lower alkyl phthalates are markedly repellent to nearly all insects.

The mode of action of pyrethrum synergists has been reviewed and discussed<sup>25</sup> and the suggestion made that they affect the orientation of the insecticide molecules at the insect nerve endings. It has been established that synergism increases until a 1:1 molecular proportion of the pyrethrins and synergist are present, when further additions of synergist are ineffective.

Terpineol<sup>26</sup> has been recommended as a synergist for technical grades of hexachloro-*cyclohexane*, but as its effectiveness decreases as the latter is purified, the mode of action is obscure.

### Stabilisation of insecticides

Attention has recently been given to the action of light on insecticides. Chisholm and Koblitsky<sup>27</sup> found losses of DDT in sunlight to be about one-fifth of the original material with crude DDT and suggested that the use of a relatively volatile diluent, *e.g.*, sulphur, might uncover fresh insecticidal surfaces. Ultra-violet light, which is especially active in decomposing derris and pyrethrum extracts, may be absorbed by a yellow dye (Chloramine Yellow G), according to M. and G. B. R. de Dominico,<sup>28</sup> who also add anti-oxidants to their preparations.

R. G. Nel and G. E. A. Mathew<sup>29</sup> have found that sunlight decomposes films of pyrethrins in white oil more rapidly than those formed with kerosene. This effect may be due to the absorption of some ultra-violet light by the conjugated constituents of kerosene, but is possibly also due to a confusion with the concentration effect caused by the relative volatility of many kerosene constituents. Certain synergists, such as piperonyl butoxide, have been claimed as stabilisers for pyrethrum preparations,<sup>15</sup> but here again confusion between synergism and stabilisation is noticeable.

Raymond and Padhye<sup>30</sup> suggest that pre-extraction treatment of pyrethrum flowers with sulphur dioxide would be effective in preserving the rather unstable active ingredients, and, indeed, many such anti-oxidants have been suggested, of which di-*tert*.butyl-*p*-cresol has useful properties.

A study of the long-term effects of storing aerosols in metal containers has been described by Fales, Nelson, Ball, and Fulton.<sup>31</sup> Their account shows that both DDT and pyrethrum retain their toxicity, when stored in solution in "Freon" (dichlorodifluoromethane) for up to five years, but that corrosion of the container is marked when DDT is included in the mixture.

### Persistence of insecticides under field conditions

Parkin and Green<sup>32</sup> have shown that the toxicity of DDT in oil, when sprayed on wall-board, is proportional to the concentration of the insecticide even when the total weight of DDT applied is kept constant.

These authors have also shown that the supersaturated solutions of DDT thus liable to be formed can be crystallised by the action of flies in walking across them. This crystallisation process, contrary perhaps to expectation, increases the toxicity of the film considerably. Such films remain toxic for at least 18 months.

The crystallisation of DDT from oil solutions on building materials has been compared to the "blooming" of sulphur on rubber.<sup>33</sup> The effect is considered to be due to a mechanism similar to that employed in preparing crystalline precipitates for filtration in analytical work.<sup>34</sup>

In a further paper, Hewlett and Parkin<sup>35</sup> showed that, with pyrethrum in oil films particularly, prolongation of the effective life was assisted by pre-treatment of a building material substrate with a substance which is both impermeable to the insecticide and wetted by it. Size and gelatin were found suitable for such pre-treatments.

Penetration of insecticides into the substrate has frequently been shown to be a major cause of the loss of activity found in most experiments after a lapse of some days after spraying. Schmitz and Goethe<sup>36</sup> have studied the penetration of DDT emulsions, and solutions in oil, into wooden surfaces. These authors consider that only the top 0.001 in. of wood contains available DDT, and find that only about a third of the DDT sprayed on a wooden surface remains in this layer.

G. E. Fogg<sup>37</sup> has discussed the penetration of the leaves of plants by 3:5-dinitro-ortho-cresol. Entry through the stomata of *Sinapis arvensis* was unimportant except by gaseous diffusion from a dried deposit; from a wet deposit the undissociated compound diffuses directly through the epidermis.

Penetration of insecticides and fungicides into plant tissue may have either beneficial or deleterious effects. If only just sufficient material has been applied, loss by penetration may lead to inefficiency, but when an excess of some suitable substance has been applied on to a part of a plant, translocation may occur to another, otherwise inaccessible, site of action. This phenomenon can be particularly important with heavily foliated plants, when insects and fungi are frequently protected from sprays and dusts on the underside of the leaves. A comparatively small translocation through the leaf may then be effective in controlling the pest.

Cattle, too, absorb insecticides more rapidly than inert substrates.<sup>38</sup>

A. B. Hadaway and F. Barlow<sup>39</sup> have carried out penetration tests of DDT on mud blocks, testing the residues against tsetse flies and yellow fever mosquitos, and also chemically determining the DDT present in the outer 0.1-mm. layer of mud. These authors found that with 5% oil-base solutions, only 6-15% of the DDT present remained in the outer layer of the mud blocks. Emulsions gave results rather better than those obtained with oil-base sprays, but suspensions of wettable DDT powders, proved most effective.

Houseflies and malarial mosquitos have been used by R. W. Fay, E. L. Cole, and A. J. Buckner,<sup>40</sup> to examine the relative residual effects of DDT, benzene hexachloride, Chlordane, Toxaphene (chlorinated camphene) and DDD (1:1-diparachlorophenyl-2:2-dichlorethane). The compounds mentioned are in order of decreasing effectiveness. Synergised pyrethrum preparations were not found effective.

### Application of insecticides

A great deal of work on the comparative toxicity of the newer chlorinated hydrocarbon insecticides has been published. In many respects this development work follows the lines of that which took place after DDT and benzene hexachloride became available in quantity, and seems to stress the important effects of the conditions of application in the field and laboratory.

R. D. Glasgow<sup>42</sup> has given a review of the methods available for the application and distribution of insecticides, and has indicated the advantages to be obtained from close control of the droplet size of sprays and aerosols, advantages made possible by recent developments on the mechanical construction of equipment. With aerosols, this particle size effect has been shown to control the rate of settling in accordance with Cunningham's correction of Stokes' law, the former factor being closely related to the effective toxicity.<sup>43</sup>

R. A. Fulton<sup>44</sup> has published an account of the propellants used in low-pressure aerosols, the fluorinated and methylated chloromethanes being the most useful substances. The same author has also given a chronological list of publications on aerosols from 1942 onwards.<sup>45</sup>

The effect of particle size has been combined with wind-tunnel experiments controlling the velocity of movement of DDT aerosols by R. Latta *et al.*<sup>46</sup>

### Diluents for toxic dusts

Although most solid insecticides are usually more effective in the field when applied in solutions or emulsions, extreme shortage of water in certain areas, or other conditions, may necessitate application in the form of dusts. In order to spread the toxic dust effectively, it must be diluted whether by mixing or by impregnation of a diluent with a solution of the toxic material. The choice of diluent is often limited by its cost at the site of manufacture or application, but the toxicity of the "inert" diluent, alone or in the finished insecticides, may sometimes be of overriding importance. Watkins and Norton<sup>48</sup> have classified mineral diluents into seven groups according to the major mineral constituent. Oxides and silicates are the most numerous. The oxides comprise silica as tripolite and diatomite and "calcium lime," containing less than 10% magnesia and "magnesium lime," containing more than 10%. The silicates are said to comprise mica, talc, pyrophyllite and three groups of clays. Hunt<sup>48</sup> has determined the toxicity of diluents under various conditions of light, temperature and humidity, to the Mexican bean beetle. Among members of the same group there were wide differences in potency, *e.g.*, among the talcs was a variation in mortality from zero to 50%. All members of the diatomite and attapulgite groups gave high kills, but botanical flours and the three forms of calcite tested gave very low mortalities. Walnut shell flour and a kaolinitic clay were tested, admixed with cryolite or rotenone at 90° F. and 38% R.H. and 75° F. and 75% R.H. At 90° F. and 38% R.H. the toxicity of clay alone approached that of the cryolite and rotenone mixtures with it and was greater than that of mixtures containing cryolite or rotenone and walnut

shell flour. It is suggested that this may be due mainly to the dessicating action of the clay, whereas the superiority of the clay-toxicant mixtures at 75° F. and 75% R.H. may be due to abrasion facilitating penetration by the toxicant. Other authors have established with rotenone the action of certain very finely ground diluents in surrounding the particles of toxicant and making them less effective.

Gooden<sup>49</sup> points out that pyrophyllite as a diluent is very variable and is easily confused with mica or talc and frequently contains quartz. Methods of distinguishing the minerals and removing quartz are given as well as the X-ray diffraction patterns for quartz and for pyrophyllite, talc, and kaolin of different degrees of purity. Wilson and Jackson<sup>50</sup> state that the efficacy of a dust varies with the electrostatic charge induced on the plant, which in turn varies with the mineral diluents in the dust, the particle size, etc. The results are to be expected from the crystal lattice constituents and the cleavage. It may be mentioned that toxicity of dusts to insects also varies with the charge.

### Spraying by aircraft

The logical extension of widespread application of insecticides from the ground is spraying and dusting operations from low-flying aircraft. The more obvious possibilities of this latter method of application are fairly well established, though many problems remain to be solved. Attention is being drawn to the detailed physics and chemistry of falling drops.

Richardson<sup>51</sup> has reviewed recent physical work on the properties of aircraft sprays, and has shown that the rate of evaporation of small drops is rather greater than would be expected from the Langmuir-Frosling expression. The same author also observed that towards the end of their fall, small droplets tended to traverse a sinuous rather than a straight path.

J. S. Kennedy, M. Ainsworth, and B. A. Toms<sup>52</sup> have carried out an extensive investigation of the interaction of oil-base sprays, containing dinitro-*o*-cresol, for application from the air against locust swarms and breeding areas, with stationary and flying insects.

The effects of the widespread application of DDT on non-insect populations, such as plankton,<sup>53</sup> and birds and mammals<sup>54</sup> have been studied, showing little detrimental effect.

On the other hand, reports are becoming available of the danger of using DDT sprays to attempt the control of insects whose numbers are normally kept down by predators. Caution is particularly necessary when dealing with hemipterous insects, most of whom feed by sucking plant juices, and which are not usually well controlled by DDT.

DDT sprays intended to control codling moth have frequently led to trouble through the elimination of the parasites of various hemiptera. For example, M. A. Yothers reports that woolly aphid is having to be controlled by special chemical means in orchards where DDT has been sprayed against the codling moth.<sup>55</sup> Formerly, the predators and parasites of the woolly aphid were often sufficient for this purpose. On citrus trees, too,<sup>56</sup> oil-base sprays and arsenicals have increased cottony cushion scale infestations by killing off the parasites. By careful timing,

the destruction of beneficial insects by DDT may be greatly reduced. Red spider, whose increase in numbers is a frequent result of spraying with DDT in citrus and other orchards<sup>57</sup> and greenhouses, may often be controlled with azobenzene.<sup>58</sup> Combined DDT and azobenzene smokes are coming into use for greenhouses, and have proved effective in such situations, particularly as azobenzene is generally ovicidal, a property not shared by many other insecticides.<sup>59</sup>

Baits containing Chlordane have also been applied from the air,<sup>60</sup> and give good control of *Melanoplus mexicanus* and one application of 5% DDT at 20 lb. per acre by aeroplane gave complete control of army worms on flax, according to J. N. Roney,<sup>61</sup> who emphasises the necessity of a prompt and rapid control measure to protect this sensitive crop.

Since some insecticides have been applied from the exhausts of aircraft, it is important to study their thermal stability. F. A. Gunther<sup>62</sup> has found that benzene hexachloride, commercial grades of which contain traces of iron, reduces the thermal stability of DDT when mixed with it. All four isomers of benzene hexachloride are stable at 120° c. but technical DDT is completely decomposed at this temperature.

### Damage to wild life, plants and mammals by DDT, B.H.C., Chlordane, and chlorinated camphene

Chronic effects of poisons take a considerable period to develop, and it is impossible to establish quickly the complete harmlessness of a new toxicant. There is now, however, considerable evidence that these newer insecticides can be used with safety under most conditions with certain reservations. Cameron<sup>63</sup> states the risk of DDT poisoning to man and mammals is slight. Storage of DDT in fatty tissues, detoxication in the liver and excretion in milk, is shown by chemical tests. Woodard<sup>64</sup> *et al.* has studied the mammalian metabolism of all four insecticides. DDT appears to be metabolised in the liver. There is a critical intake level above which storage occurs, rising to a steady value corresponding to the rate of intake, after about 50 days. The toxicity of chlordane and DDT to white rats has been determined by Ingle.<sup>65</sup>

Residues of insecticides on food crops and forage crops are important. Carter<sup>66</sup> gives figures for DDT residues on apples and peaches, and figures for DDT in fat and milk and eggs of animals fed on treated fodder. Wilson, Allen, Bohstedt, Bethel, and Lardy<sup>67</sup> have fed cows, sheep and rats on DDT-treated silage and determined the proportion of DDT in various tissues. (See also Lardy.<sup>68</sup>)

Stoker<sup>69</sup> has studied the phytotoxicity of DDT and BHC. Spraying with DDT damaged cucurbits but not tomatoes or summer cabbage. BHC sprays did not affect tomatoes, but high concentrations scorched radish, turnip, swede, kale, spinach, and beet seedlings. A dispersible BHC powder spray tainted potatoes, peas, carrots, beet, marrows, cauliflowers, and lettuce. Sprayed apples and plums developed taint after cooking. Several workers report a reduction of percentage germination of seeds treated with BHC, *e.g.*, Brooks and Anderson,<sup>70</sup> Grayson and Poos.<sup>71</sup>

### The mode of action of contact insecticides

Although it can scarcely be said that the mode of action of many of the more important insecticides has been established unequivocally, much research and thought have been stimulated by this and allied problems.

According to Yun Pei Sun and R. Hansberry,<sup>72</sup> the liquids known as "Velsicol" solvent-insecticides, which mainly contain highly methylated naphthalenes, act largely through the tarsi of the insect. With rotenone, on the other hand, the same authors consider that the whole body surface may be the site of action.

A clue to the mode of action of the pyrethrins may be obtained from the work on pyrethrum synergists<sup>9</sup> quoted elsewhere. In this connection it may be of significance that the active principle of *Heliopsis longipes*<sup>73</sup> which has been identified as *N-isobutyl* 2 : 6 : 8-decatrionoamide, has a similar, but otherwise unusual, structure to the well-established pyrethrum synergist *N-isobutyl* undecaenoamide.

The effect of the organic phosphorus insecticides are discussed in the section of this report devoted to them.

Turning to the chlorinated hydrocarbons, such as DDT, benzene hexachloride, and their newer competitors "Toxaphene" (chlorinated camphene) and "Chlordane" (1 : 2 : 4 : 5 : 6 : 7-hexachloro-4 : 7-dichloro methylene 3' : 4' : 7' : 7'-tetrahydroindane) the theories concerning their action have settled down into two broad groups. Firstly, in point of time, is the conception that halogenated hydrocarbons are toxic when, assuming that they are capable of transportation to the appropriate sites of action, dehydrohalogenation can take place at the site of action. The other hypothesis compares the action of these insecticides to the competitive inhibition of *p*-aminobenzoic acid by sulphonamides. References to these theories are included in the two previous reports.

With respect to benzene hexachloride, such antagonism was demonstrated with the "gamma"-isomer and fungal cultures by H. W. Buston, S. E. Jacobs, and A. Goldstein.<sup>74</sup> It has perhaps been insufficiently appreciated that insects have well developed nervous systems which are not possessed by fungi and that the chlorinated hydrocarbons may act as nerve poisons at lower dosages than those at which the inhibition effect could occur. R. L. Metcalf,<sup>75</sup> for example, has found that with thrips, the most potent of the insecticides tested was the "gamma" isomer of benzene hexachloride, but that *meso*-inositol had no effect on its toxicity.

It has, however, recently been demonstrated by G. W. van Vloten *et al.*<sup>76</sup> that the "gamma" isomer of benzene hexachloride has a different structure from that assigned to it earlier, the structure now assigned being one that was earlier considered rather unlikely to exist on stereochemical grounds. It appears<sup>77</sup> that the isomer of benzene hexachloride corresponding to *meso*inositol is, in fact, the *delta*-isomer, this compound having the structure previously assigned to the "gamma"-isomer.

In this connection it is interesting to note that the "*delta*"-isomer has been found more toxic than the "*gamma*"-isomer (on the old terminology) to snails of the genera *Planorbis* and *Bulinus*.<sup>78,79</sup> This finding is of

particular importance in view of the fact that these snails are intermediate hosts of the *Bilharzia* parasite, and thus vectors of schistosomiasis in Egypt and other parts of the world.

J. K. Wilson and R. S. Chaudin<sup>80</sup> have recently demonstrated that the "*delta*"-isomer is also rather more toxic to an algal growth, *Chlorella vulgaris* than the "*gamma*"-isomer.

Of the newer chlorinated hydrocarbons, the terpinoid derivatives bornyl chloride, dipentene dihydrochloride, 2:6-dichlorocamphene, and 2:6-dichlorocymene have been discussed from the point of view of toxicity in relation to the ease of dehydrochlorination.<sup>81</sup> H. Hurst<sup>82</sup> has described the action of DDT on the stability of the lipoproteins in insect cuticles, and ascribes the lethal action of the insecticide to an irreversible structural change in these substances.

H. Martin<sup>83</sup> has restated the principles on which the dehydrochlorination hypothesis rests, in the light of more recent evidence and points out that in assessing insecticidal potency, the type of insect studied has a bearing on the results obtained.

### Resistant strains of insects

Housefly and other insect populations may, by differential survival of abnormally resistant individuals, breed out a strain resistant to some particular insecticide. This phenomenon has long been known with scale insects surviving fumigation by HCN on citrus and other trees. Recently contamination of a laboratory with hexachloro-*cyclohexane*<sup>84</sup> has caused a six-fold increase in the median lethal dose of this insecticide for houseflies. The same authors were also able to obtain a two-fold increase in the resistance of flies to lethane, an aliphatic thiocyanate derivative, and found that flies bred out as resistant to benzene hexachloride were also resistant to other insecticides.

G. W. Barber, O. Starnes, and E. B. Starnes<sup>8</sup> have bred strains of houseflies resistant to DDT and pyrethrum, but the design and analysis of their experiments is open to criticism.

Certain blue cattle ticks, which had acquired resistance to arsenical cattle dips through breeding from survivors were, however, successfully controlled with benzene hexachloride.<sup>86</sup> Sub-lethal doses of pyrethrum on cigarette beetles reduced the subsequent oviposition by the females.<sup>87</sup>

### Chemical control of non-insect pests

Many insecticides offer effective control of such pests as mites, slugs, snails, etc., although the major differences in the physiology of such organisms renders any generalisation dangerous.

An interesting case arises from the determination of the relative toxicities of the isomers of benzene hexachloride to snails, from which it was deduced that the *delta*-isomer, rather than the *gamma*-isomer was the most toxic (see section on "Mode of action of insecticides").

DDT, benzene hexachloride, and nicotine may all be used to control the red-legged earth mite,<sup>88</sup> and the first-mentioned insecticide is also useful against Pacific mites.<sup>89</sup> On the whole, however, chlorinated hydrocarbons are ineffective against mites, ticks, etc., and red spider

mite is particularly hard to control by these means. Crude tetra-ethyl pyrophosphate shows some promise in this direction, however.<sup>90</sup>

H. G. Fluno, H. A. Jones, and F. M. Snyder<sup>91</sup> have discussed the use of various emulsifiers for preparing acaricides, and polychloro-cyclane sulphides are said to be more effective acaricides than the halogenated hydrocarbon base alone.<sup>92</sup>

## Fumigants

Fumigants, insecticides which act in the vapour phase, have not received much attention in these reviews in recent years, and it appears desirable to consider work dating from a few years back. The number of useful fumigants is small, compared with other classes of insecticide, being limited by the requirement of a considerable vapour pressure. Other requirements are toxicity to the pest, safety and convenience in handling, freedom from phyto-toxic effects to foodstuffs or other materials by poisoning, tainting, etc. In addition, a low sorption from the vapour is highly desirable.

Many of the older fumigants are still in use, *e.g.*, hydrogen cyanide, ethylene oxide, carbon tetrachloride, and ethylene dichloride and ethyl formate, in the more developed parts of the world, and carbon disulphide in the less developed. Newer and more specialised fumigants are methyl bromide, ethylene dibromide, trichloroacetonitrile (trichloromethyl cyanide), dichloropropylene and dichloropropane, and dichloro-diethyl ether. Fumigants with lower vapour pressures include the five older ones, naphthalene, the dichlorobenzenes, nicotine, tetrachloroethane, and mercury, and the newer ones, BHC and Chlordane.

Early work with fumigants was done mainly by rule of thumb and rapid improvement was to be expected only when chemical methods of assessing a fumigation had been developed and applied. A review of improvements up to 1939 and an outline of some experiments then in progress was given by Page and Lubatti.<sup>93,94</sup> Further progress has been largely along the lines indicated in these papers, absorption of fumigants having been most intensively studied in this country and the application of chemical assessment having made some progress in America and elsewhere.

A good deal of recent work remains, as yet, unpublished.

Methods of application have remained simple and rely on atomisation of the liquid fumigant, evaporation from an absorbent preparation or, in the case of hydrogen cyanide, interaction of calcium cyanide or a mixture of sodium cyanide and magnesium sulphate with water vapour in the air. The latter method is advantageous where liberation at a large number of points is necessary, *cf.*, the fumigation of grain in silos with granular calcium cyanide, or where a prolonged liberation is desirable, as, for example, in the fumigation of rabbit burrows, Southern.<sup>95</sup> More elaborate methods are used only when certainty and rapidity of vaporisation are required as, for example, in chambers where the best use must be made of expensive plant and in the fumigation of citrus trees under tents where rapidity is essential. In fixed plant, water-jacketed vaporisers, heated by electricity or coal gas are employed and are often inserted in the circulatory system. For citrus trees a flash boiler fired with oil and a pump delivering a given amount of liquid hydrogen cyanide at each

stroke is much used. The older absorbent preparations, such as hydrogen cyanide in porous granules of gypsum or kielselguhr or cellulose discs are still in use but, as yet, new ones are not available. Smokes from the combustion of impregnated paper or of cartridges containing the insecticide are used for nicotine and for BHC but the vapour pressure of the latter is probably too low for use as a space fumigant at normal temperatures and the method serves mainly to effect distribution in a finely particulate form. Soil fumigants, an excellent compilation of which is given by Gough,<sup>96</sup> are sometimes formulated as emulsions with a view to securing better distribution and delayed vaporisation.

The advantage of stirring during most fumigations is becoming apparent, an even distribution in the free space is thereby secured and, if the stirring is sufficiently powerful, improved penetration of goods. In chambers the stirring is circulatory, and by means of valves, the fans and ducts are also used, at the end of the fumigation, to provide rapid airing. Greater safety and efficiency are thereby secured. It is safer to keep the trunking, etc., used during fumigation wholly within the chamber and to reduce the external trunking used for airing to a minimum. Unloading can safely be started after a very short period of airing if the place where men are working is swept continuously by fresh air by means of properly arranged ducting and fans, Page, Lubatti, and Russell,<sup>97</sup> Page and Lubatti.<sup>98</sup> Ventilation of barges and other temporary storages employed for fumigation can be improved by the use of a large mobile centrifugal fan with lengths of canvas hose which enable the barges to be cleared of gas by blowing. A vaporiser is conveniently mounted alongside the fan. The liquid fumigant in the pipe-line from the cylinder to the vaporiser or the atomising jets in the barge, etc., is of necessity under a considerable pressure, whereas the pressure of the gas leaving the vaporiser is only slightly above atmospheric. Therefore the joints in the liquid line need to be much better than those in the gas-line and, in many circumstances it is safer and more convenient to use a vaporiser close to the cylinder and to carry the fumigant to the barge, etc., in the form of vapour. For this latter purpose lengths of hose, preferably solvent resistant, are suitable, being cheap, flexible, and easy to handle.

Vacuum fumigation in chambers from which most of the air is removed by a pump prior to admitting the fumigant are used in small numbers with the object of rendering the fumigant more toxic or of improving penetration. The former object is, theoretically, attainable if the optimum oxygen deficiency for the species is known and the second is attainable only if the main hindrance to penetration is mechanical and if the fumigant is only slightly sorbed. A recent publication is that by Monro.<sup>99</sup> Vacuum fumigation, whatever its merits, is not adapted to the handling of really big tonnages which must be treated in ships, barges, railway box-cars, warehouses or chambers used at atmospheric pressure. Under these conditions hydrogen cyanide and ethylene oxide plus carbon dioxide are still good fumigants whilst methyl bromide, which carries a special poison hazard and needs more careful sealing to prevent leaks, is gradually coming into use, particularly in Canada and the U.S.A., Monro and Delisle,<sup>100</sup> Monro.<sup>101</sup>

The application to soil has received most attention in the U.S.A. where large, multiple drill, tractor-drawn machines, have been developed. The liquid is measured out evenly to each tine by an adjustable pump mechanism and there is often a trailing roller or other device for closing in the drill after the fumigant has been injected. Sometimes the ground is also consolidated afterwards by a separate, power-driven roller.

Lateral dispersion of the fumigant may be improved by application after discing, Carter.<sup>102</sup> The efficacy of the various methods of application, in the field, varies with the soil type and condition. Chemical measurements of dispersion have been made by Higgins and Pollard.<sup>103,104</sup> Most investigations have relied on insecticidal effects, *e.g.*, Fleming and Baker.<sup>105</sup> Recently, Schmidt<sup>106</sup> has studied the dispersion of "D.D." and of chloropicrin from a single injection point in soil of various water contents contained in a large box. The mortality of rice weevils in cages was used as a criterion of concentration of gas. The results appear to show that chloropicrin is more readily dispersed and retained for longer times than "D.D.," and that dispersion is most rapid and retention longest with soil of median water content. The latter observation may be related to the observation of Lubatti and Smith<sup>107</sup> of a minimum in the curve for sorption and water content of soil.

Whilst even distribution of fumigant can readily be achieved in "space" fumigation any adequate control of distribution in soil fumigation is difficult. In particular, the concentration at the surface of the soil is extremely low. The time concentration curves at other points are a function of the composition, character, and water content of the soil, and the composition of the fumigant as well as the method of injection. Not much systematic work has been attempted. Treatments in the open have given variable results which are complicated by "soil amendment" or alteration in the micro-biology. This will often give an increase in yield of crop accompanied by a net increase rather than a decrease in population of the soil pest, which remains, therefore, a menace for future years. More satisfactory results are often obtained in the fumigation of soil in glasshouses. Here the texture, character and water content are under some control, the effect of unsuitable weather is ruled out and the surface can be covered with a relatively gas-tight paper during fumigation in an attempt to secure higher surface concentrations. The soil fumigants most used are carbon disulphide, chloropicrin, ethylene dibromide, and "D.D."—an impure mixture containing 1:2-dichloropropane; 1:3-dichloropropene, trichlorides, and higher boiling fractions.

With mixed fumigants synergistic effects are probable and "fractionation" in the soil produced by differences in volatility, rate of movement, and fixation by sorption, coupled with problems of analysis render chemical assessment of behaviour difficult.

Methyl bromide is used for fumigation in glasshouses whilst B.H.C., chlordane and emulsions of ethylene dibromide (Lange,<sup>108</sup> Mason and Chisholm,<sup>109</sup> and Newhall<sup>110</sup>), are applied to the surface of the soil and act as local fumigants.

Mercury is an unusual type of fumigant, and its use is likely to be restricted to the fumigation of grain in small silos. So far it has been applied in the form of porous bricks containing mercury droplets,

Wright,<sup>111</sup> and of amalgamated copper plates, Dole.<sup>112</sup> It is extremely toxic to eggs of the grain weevil, Richards.<sup>113</sup> The toxicity increases markedly with temperature over the range 10° to 25° so that fumigation with mercury is likely to be of most use in hot countries. It has long been used in India. It has the advantage of contact dusts that continuing protection is provided so long as the grain remains in the silo. It has also the advantage of other fumigants that there is no trouble in mixing when the grain goes into store and no cleaning when it comes out.

The sorption of fumigants by solid or liquid substances is important for two main reasons, it leads to a reduction of concentration of gas and it may harm the sorbent. The reduction of concentration brought about by sorption often exceeds that brought about by leaks. Inside bags, bales, etc., the reduction depends partly on sorption and partly on the hindrance to convection offered by the method of packing and stacking. Where the hindrance is great the rate of penetration is governed by it, and the reduced internal concentration may be approximately uniform throughout the package. Where the hindrance is small there is often a very steep internal concentration gradient.

The small degree of sorption of methyl bromide by most substances, compared with the sorption of fumigants such as the chlorinated hydrocarbons, hydrogen cyanide, and ethylene oxide, results, in general, in greatly improved penetration, see, for example, Brown and Lewis.<sup>114</sup>

The magnitude and rate of sorption depend on a number of physical conditions and on the chemical properties of the sorbent and the fumigant.

Reversible sorption may sometimes be advantageous however, as it provides a "reserve" of fumigant which is gradually desorbed as the free space concentration is reduced by leakage.

The recent advances in our knowledge of the sorption of fumigants are due mainly to Lubatti and co-workers, and to Winteringham, Lewis, and co-workers; Winteringham,<sup>115</sup> the sorption of ethylene dichloride by wheat products. Winteringham,<sup>116</sup> method for the micro-determination of the sorption of fumigants. Lewis and Eccleston,<sup>117</sup> residues in wheat flour fumigated with methyl bromide. Winteringham and Harrison,<sup>118</sup> the sorption of methyl bromide by wheat. Lubatti,<sup>119</sup> sorption of hydrogen cyanide by wheat. Lubatti and Harrison,<sup>120</sup> comparison of the sorption of hydrogen cyanide, ethylene oxide, trichloroacetonitrile (trichloromethyl cyanide) and methyl bromide by wheat. Lubatti and Smith,<sup>121</sup> sorption of methyl bromide by onion seed. Lubatti, Russell, and Porter,<sup>122</sup> a fumigation chamber for onion seeds. Lubatti and Smith,<sup>123</sup> sorption of methyl bromide by potatoes. The sorbents, which include also soya beans, sultanas and ground nuts, contain a wide variety of chemical compounds, and are all organisms of which the physical structure, enzymic activity, etc., vary with variety, maturity, water content, and temperature.

In all systems sorption at the beginning of the fumigation is mainly physical. Sometimes, as with hydrogen cyanide on wheat, this is followed by very little chemical action. There is an asymptotic approach to apparent equilibrium and most of the fumigant sorbed can be recovered on airing. The temperature coefficient is negative, and the rate of sorption is governed by a physical factor such as diffusion. In this

particular system it is possible to evaluate a constant transference coefficient on the assumption that the main barriers to diffusion are the seed coats and, by substituting in an expression based on Fick's law, to fit a theoretical curve quite accurately to the experimental values. Even with this system there is some irreversible chemical action, mainly with the bran, the suggestion having been made that additive compounds with the furans are formed, analogous to the cyanohydrins formed with reducing sugars. With other systems, such as ethylene oxide and wheat or methyl bromide and onion seed the fumigant reacts after sorption, and a steady state is soon reached when the rate of sorption is equal to the rate at which the fumigant arrives at the site of action. If the external concentration is maintained the total amount of fumigant removed from the gas phase as well as the amount reacting with the solid increase linearly with time. The temperature coefficient is positive owing to the increase in the rate of removal of fumigant by chemical action.

The effect of moisture content on sorption by seeds is complex. Starting with rather dry seed the sorption falls at first (*e.g.*, Winteringham and Harrison, *loc. cit.*), as the moisture is increased, but with further increase in moisture the sorption passes through a minimum and rises, often asymptotically, to a steady value. As the seed becomes really wet, there may be a further slight decrease in sorption (*e.g.*, Lubatti and Smith, *loc. cit.*). The minimum occurs at or near the critical water content of the seed, above which it cannot safely be stored for extended periods. It is suggested by Lubatti that the initial decrease is caused by sorption of water on the pore surface of the cellulose micelles which results in a decrease in permeability of the seed coats. It is thought that the rise which occurs beyond the critical moisture content may be due to a re-orientation of the micelles and a loosening of the membrane structures or to a separation of the cellulose chains composing the fibres by the sorption of the water molecules between them. Whilst the moisture content of the seed coats appears to be the principal factor governing the behaviour of the seed to fumigants that of the other tissues also has some effect. At high water contents the whole seed is so permeable that the sorption is the same as that with ground seed. With viable sorbents the increase in sorption which goes with increase in water content beyond the critical point, is accompanied by damage such as retardation of germination of seeds or reduction in the percentage germination. In this range too, there is generally an increase in chemical action. Similarly, a rise in the temperature of fumigation is detrimental, probably, owing mainly to the increased rate of chemical reaction.

Foods, seeds, etc., may be damaged in various other ways by fumigation, Page and Lubatti.<sup>124</sup> A change in odour, flavour or appearance may be produced which is often referred to as taint. Generally, this can be detected only by properly designed physiological tests. Taint may be derived indirectly as in eggs, milk, and meat from animals whose food has been fumigated with chlorinated aromatic hydrocarbons, or in tubers or fruit grown on soil previously fumigated with impure dichloro-propylene and dichloro-propane mixtures. The tainted produce has a greatly increased chloride content. Only a few of the chemical actions which occur during sorption have been studied. In the fumigation of

dried fruit with hydrogen cyanide the cyanohydrin of laevulose but not that of glucose is formed, Turtle.<sup>125</sup> The compound is as toxic as the equivalent weight of free hydrogen cyanide. Ethylene oxide is supposed to react with certain proteins or similar compounds. More attention has been given to the reactions of methyl bromide, a fumigant which combines high toxicity to insects with good penetration, which is associated with its small total sorption. Curiously, however, of the small amount sorbed, a very high proportion reacts chemically with the sorbent. In onion seed it probably reacts either with a sulphide or disulphide, the reaction being catalysed by the mercuric ion, so that seed to be fumigated must not be treated with calomel. In certain foods, starch, wheat, peas, and soya beans, the amount of methyl bromide reacting is proportional to the nitrogen content, Lewis and Eccleston (*loc. cit.*), Russell,<sup>126</sup> and Murray,<sup>127</sup> have investigated some of the reactions of methyl bromide with certain organic nitrogen compounds. Pyridine bases react fully at neutrality or slight acidity to form quaternary pyridinium compounds. Nicotinic acid is also said to react fully under these conditions. Reaction may occur with primary, secondary, or tertiary nitrogen, 3, 2, and 1 molecules of methyl bromide reacting respectively per atom of nitrogen. Amino acids require addition of alkali. The methylation of the thiol group in cystein and in reduced glutathione by fumigation with methyl bromide is rapid and nearly quantitative according to Lewis.<sup>128</sup> The enzymic activity of papain in its reduced form, containing -SH groups, is inhibited by methyl bromide fumigation. Other enzyme systems behave similarly, *e.g.*, urease, succinic dehydrogenase and certain systems concerned in the respiration of yeast. Lewis<sup>129</sup> has also demonstrated the reaction of methyl bromide with methionin. It is obvious that fumigation with methyl bromide may, under some conditions, spoil vitamins and similar compounds. Further work appears to be necessary with this and other fumigants. The amount of sorption and chemical action actually occurring can be limited by ensuring certain conditions during fumigation, Page and Lubatti.<sup>94</sup>

Advances in the use of fumigants depend on good methods of determining them both in the vapour phase and sorbed on solids. A discussion on methods of collecting gas samples is given by Page and Lubatti,<sup>97</sup> and a method of determination of residual ethylene oxide in wheat by Lubatti.<sup>130</sup>

Importance attaches to the determination of halogenated organic compounds used as fumigants. Three methods have been described, in each of which the halogen is converted into inorganic halide. Williams and co-workers, for methyl bromide, employ pyrolysis in a quartz tube at 800° in the presence of hydrogen. Winteringham has described a pyrolytic method and hydrolytic methods for chlorinated hydrocarbons,<sup>132,133,134</sup> In the latter a monoethanolamine-dioxan mixture is used. Lewis,<sup>135</sup> for methyl bromide, uses either a solution of monoethanolamine in dioxan and titrates by the method of Volhard, or a solution of sodium methoxide in methyl alcohol and titration with silver nitrate with eosin as indicator, or the procedure of Kolthoff and Yutzy.<sup>139</sup> Lubatti and Harrison<sup>136</sup> make use of catalytic combustion on an incandescent platinum wire. This method in the "flow" form is of very

general application. All fumigants are more or less toxic to man and it is necessary to determine them at low concentrations, of the order of 2 to 0.02 mg. per litre. This is particularly important with methyl bromide, which is dangerous over a wide range of concentrations when it cannot be detected by odour, etc. Litre samples can be taken, the methyl bromide burnt catalytically and the inorganic bromide determined as recommended by Russell,<sup>137</sup> who uses either the Kolthoff-Yutzy modification of van ter Meulen's method or Mohr's method with an electro-metric determination of the end-point. In a method due to Lubatti,<sup>138</sup> a stream of the atmosphere containing the methyl bromide is passed by convection over a glowing platinum wire and the bromine determined colorimetrically by the formation of eosin on a fluorescein test paper and comparison of the colour with a standard.

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# AGRICULTURE AND HORTICULTURE— INTRODUCTION

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THE scope of this section of the Annual Reports has been extended considerably this year. For the first time it has been prepared by a number of specialist reporters from among members of the Agricultural Group of the Society.

The importance of present-day problems in livestock feeding has been recognised by the long over-due inclusion of this subject in the Report. War and post-war periods have led to a reconsideration of standard levels of animal nutrition, to the employment of a number of feeding stuffs not previously in common use and to a closer examination of the economic significance of various "supplementary" foods.

The remarkable advances made in recent years, in animal medicine, also demand attention, and the uses and effects of some of the newly-developed veterinary medicines have been considered.

Among horticultural subjects the many and varied uses to which growth-regulating substances may be put continues to be one of the foremost subjects under investigation. The function of "trace elements" in plant nutrition and means of detecting a deficiency or excess of these elements in soils and plants also forms the subject of a considerable proportion of recorded literature in the period under review.

The general chemistry of insecticides and fungicides is discussed in another section of the Report, but it has seemed desirable in this section to record some recent developments in methods of application of these materials for agricultural and horticultural purposes.

Investigations of farm crops have been largely concerned with the vital problems of grassland management, and the production of cereal and oil-bearing crops.

Possibly the greatest immediate problem of the fertiliser industry is the over-all question of meeting the ever-increasing demand for their products; the more specialised investigations include many concerning the granulation of fertilisers and the related problem of placement in soil, and also the production of new forms of fertilisers either in replacement of or as supplementary to those to which we have become accustomed.

Physical aspects of soil, notably those concerned in soil-water relationships and affecting the water supply to growing crops afford much scope for continued investigation. This is emphasised by the increasing appreciation of the prime importance of water supply, in our capacity for food production.

Following the practice of recent years the Report covers a number of subjects to which research workers have more especially devoted their attention recently, and makes no claim to be of a general nature. Space restrictions and the irregular, though improving, flow of scientific literature, in themselves prevent justice being done to more than a limited

number of topics. In dealing with these, too, reference has perforce been made to communications appearing, in some cases, several years before that period strictly under review. Only in this way can current research be placed in its true perspective.

## SOILS (A. H. Cornfield)

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### Soil-water relations

A NUMBER of new techniques for the study of soil-water relations and their effects on plant growth have been developed. A. S. Hunter and O. J. Kelley<sup>1</sup> have developed a method for studying the absorption of moisture and nutrients from the soil by plant roots. Plants are grown in the soil which is packed in wooden containers  $6 \times 6 \times 72$  in. high in layers separated by tarred cheese cloth. The cloth permits penetration of roots but restricts the passage of nutrients and water from section to section. Changes in water content were measured by means of tensiometers and Bouyoucos blocks. Guayule plants absorbed water from the soil 48 in. below the surface and transported it to surface layers in which the water content was less than that at the wilting point.

The field capacity is the upper limit of soil moisture content under field conditions, and is an important soil-water characteristic. E. A. Colman<sup>2</sup> describes a simple method for carrying out the determination. He found that if small soil blocks were drained on a porous ceramic cell under a moisture tension of one-third atmosphere the moisture retained in the blocks could be related empirically to the field capacity of the same soils determined under natural field conditions.

L. A. Richards and L. R. Weaver<sup>3</sup> describe a sorption-block moisture meter which is based on weighing a porous ceramic block which has been in contact with the soil, without removing the block from the soil, thus eliminating losses due to evaporation. Hysteresis effects were obtained, but since these were in the same phase as hysteresis in the soil, the block weight more nearly corresponded with the soil moisture content.

The loss of water by lateral movement when studying infiltration rates in the field is a well-known source of error in this determination. F. L. Duley and C. E. Domingo<sup>4</sup> describe a method of reducing this error by means of buffer areas. Large plots are used which are surrounded by a buffer watered area and also by a pre-wetted belt in order to protect against loss of water by lateral seepage. A small plot placed in the middle of the large plot was found to give results very similar to that from the large plot. Similar small plots placed in the open field took up 75% more water than did the buffered plot, indicating that considerable lateral movement of water had taken place.

The difficulty of uniformly wetting a soil to any desired moisture content, especially at low moisture contents, is well known. E. Shaw<sup>5</sup> solves the problem satisfactorily by adding the water as ice scorings or snow to the dry sieved soil at  $-20^{\circ}\text{C.}$ , the process being carried out in a sub-freezing atmosphere, followed by mixing and then allowing the

mixture to reach room temperature. Moisture determinations on aliquots of a soil treated thus showed very uniform wetting.

Further work on the effects of mulching and other treatments on the rate of drying out of soils and on water movement has been carried out. E. James<sup>6</sup> studied the moisture contents at various times after initial saturation of a bare soil as compared with the same soil under a straw mulch and under a dust mulch. At the 6-in. depth, the moisture content of the straw-mulched soil remained nearly constant for 90 days after initial saturation whilst the moisture contents of the bare and dust-mulched soils decreased rapidly after approximately 25 days to the wilting point and below at almost identical rates. At the 18-in. depth the moisture contents under all three treatments were similar at a constant level for about 50 days, after which the moisture contents of the bare and dust-mulched soils diminished, the former more rapidly. The temperature differences between the various treatments were  $1.7^{\circ}\text{C}$ ., the temperature under the straw being the least. The differences were not considered sufficient to account for differences in moisture content.

L. M. Turk and N. L. Partridge<sup>7</sup> studied different types of mulching materials and found that for reducing the loss of moisture from a sandy loam the materials in decreasing order of effectiveness were: straw, maize stover, lucerne, shavings, gravel, sawdust, and peat. A. F. Pillsburg<sup>8</sup> found that infiltration was markedly reduced when an organic mulch or crop residue was placed on the surface of a loam and left to decay. Permeability was increased in the first 2 in. by irrigation following hand cultivation, was decreased by shading, and was not significantly affected by removing the  $\frac{1}{2}$ -in. surface layer of soil. Infiltration was reduced when a crop residue was burned on the surface. The application of 100 lb. per acre of nitrogen as ammonium sulphate or sodium nitrate to irrigation water containing approximately 250 p.p.m. of total solids had no effect on permeability.

### Copper in soils

The importance of copper as an essential plant nutrient and the fact that certain soils are deficient in the element has received attention from a number of workers. L. K. Wood<sup>9</sup> determined the amounts of copper extracted from soils by various reagents. Exchangeable copper, as determined by leaching with neutral normal ammonium acetate, ranged from 0.16 to 0.60 p.p.m. Total extractable copper, determined by boiling with successively stronger nitric acid, up to 10-N, ranged from 23 to 57 p.p.m. Total soil copper, as determined with perchloric acid and hydrofluoric acid, averaged about  $2\frac{1}{2}$  times the total extractable copper.

The close relation between copper and the organic matter in soils is pointed out by J. M. Bremner, P. J. G. Mann, S. G. Heintze and H. Lees<sup>10</sup> and by C. Hurwitz.<sup>11</sup> The former workers found that among certain reagents such as 0.2-M sodium pyrophosphate, orthophosphate, citrate, malate, etc., which were good extractants of copper (and other polyvalent metals) were also good extractants for organic matter. When the extractants were dialysed to remove the metal and a further amount of metal added there was an immediate precipitate of an organo-metallic

complex which showed the same type of solubility curve as did the compounds originally present in the soil. They advance the theory that part of the copper exists as co-ordination complexes with organic matter, thus rendering it insoluble in water and in neutral solvents which do not themselves form complexes with the soil. Hurwitz<sup>11</sup> found that the amount of copper which could be leached from a soil by neutral normal ammonium acetate increased as the amount of lucerne meal or oat straw which had been steeped in the extracting solution increased. Inorganic copper was not affected by the treatments. He considers that the copper which is affected exists as an organo-copper complex. From the practical point of view since moisture and crop residues are highest in spring and autumn organic copper may then be converted to soluble inorganic form, thus replenishing the available copper in the soil. The inorganic copper may take part in exchange reactions.

Wood<sup>9</sup> considered that 0.1 to 1 p.p.m. of exchangeable copper was sufficient for normal growth of plants. Under certain conditions the copper added to soil becomes fixed in forms which are not available to plants. Wood obtained an erratic response by plants to copper added to the soil, this being considered due to fixation. Fixation took place when the soil was alternately wetted and dried and also when subjected to moist storage. B. Arenz<sup>12</sup> found a variable response by different plants to additions of copper to a soil considered to be deficient in the element. Copper additions were needed to produce normal growth of potates and oats, but were not needed for dwarf beans. The lasting effect of the copper depended on the manner in which it was added. When added as copper sulphate there was no effect on potatoes after three years, but when added as a copper-containing iron oxide sludge the effect on both quality and yield of the crop was still apparent after three years.

An interesting relationship between copper and manganese in the soil is pointed out by G. D. Sherman, J. S. McHargue, and W. S. Hodgkiss.<sup>13</sup> They found that whereas liming an acid soil, which was initially low in active manganese, caused the appearance of grey speck in oats, the addition of very small amounts of copper sulphate with the lime prevented development of the disease, indicating that the copper had retarded the oxidation of manganese to insoluble forms. Similarly, the depression of exchangeable manganese due to liming was reduced in the presence of copper. H. Lees<sup>14</sup> considers that copper may be an important factor in soil nitrification. He found that a fen soil lost its power of nitrification on treatment with sodium diethyldithiocarbamate, but regained it when subsequently treated with copper.

### Manganese in the soil and its relation to plant growth

Further work on the relation of soil manganese to plant growth, methods of control of deficiencies or excess of the element and methods of determining the manganese status of soils has been carried out.

G. D. Sherman and P. M. Harmer<sup>15</sup> found that when the exchangeable manganese of soils, as determined by leaching with neutral normal ammonium acetate, was greater than 3 p.p.m. there was sufficient available manganese to prevent the appearance of grey speck in oats,

but found no relation between control of the disease and either water-soluble or Leeper's "active" manganese (manganese extracted by quinol in a neutral solution). G. W. Leeper,<sup>16</sup> in a review of his method for determining available manganese, concluded that the test was useful for indicating the ability of most soils to supply manganese, though some soils which were high in "active" manganese were associated with deficiencies, whilst others with less active manganese were free from it. He considers that no single test can distinguish between healthy and deficient soils. M. H. McVickar<sup>17</sup> found that there was no relation between the uptake of manganese by Kentucky bluegrass and total soil manganese, manganese as manganese dioxide or available manganese (which he considers to be the sum of the replaceable manganese and manganese as manganese dioxide). He found that uptake of manganese was influenced by  $p_H$ , organic matter, and aeration. A. W. Marsh and W. L. Powers<sup>18</sup> showed that plant analysis was a useful indicator of manganese deficiency. They found for a number of crops that when the manganese content of the leaves fell below 100 p.p.m. response to additions of manganese to the soil was obtained.

Application of manganese sulphate to the soil still appears to be the usual method of controlling manganese deficiency, but Sherman and Harmer<sup>15</sup> show that where there was sufficient manganese, present in an unavailable form in an alkaline organic soil, application of sufficient sulphur to reduce the  $p_H$  below 7 was a satisfactory method of controlling grey speck in oats. Treatment of the soil with quinol, creatinine, haemoglobin, stannous chloride, or sodium bisulphite was as effective as manganese sulphate for controlling the disease. J. D. MacLachlen<sup>19,20</sup> compared a number of treatments for controlling grey speck in oats. He found that only relatively heavy applications of manganese sulphate to the soil would control the disease but when sulphur was applied at the same time the manganese sulphate requirements were reduced. Spraying the plant with 1 to 2% solutions of manganese sulphate eliminated deficiency symptoms and increased yields but caused a certain amount of leaf scorch, whilst dusting with manganese sulphate caused severe foliage injury. Soil treatments with manganese ores, containing 7-30% of manganese, were ineffective in controlling the disease.

E. H. Kipps<sup>21</sup> reports a case of poor growth of lucerne which was traced to a high level of exchangeable manganese accompanied by a low level of available calcium in the soil. Growth was improved by increasing the degree of base saturation and raising the  $p_H$ , by which manganese availability was reduced. Healthy plants had a Ca : Mn ratio greater than 66 : 1.

R. H. Hageman, J. S. McHargue, G. D. Sherman, and E. S. Hodge<sup>22</sup> have shown fairly conclusively that the grey speck disease of oats is due to manganese deficiency. By growing oats in sand cultures which were free of manganese, symptoms of grey speck, identical with those produced in manganese-deficient soils, were produced. A manganese level of 2 p.p.m. in the culture solution was sufficient for normal growth. A. W. Marsh and W. B. Bollen,<sup>23</sup> in a study of the effect of manganese additions on the microflora and respiration of soils, concluded that increased growth of plants due to manganese additions to the soil resulted from a

direct effect on plant nutrition rather than from any indirect microbial reactions.

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## FERTILISERS (D. P. Hopkins)

### Manufacture

THE outstanding fact about fertiliser manufacture is that it can never catch up with the demand. Production of fertilisers generally is expanding each year, often exceeding the most optimistic targets. But the demand also increases so that the gap remains as wide as before. Estimates that production and demand may balance within a few years seem somewhat bold unless the world is going to ignore the warnings of FAO and Boyd Orr; any serious attempt to double world food production during the next 25 years inevitably calls for very large annual increases in the tonnage of fertilisers applied. It is also true, however, that fertiliser demand is closely related to farm income. In countries where farm produce and farming commodities are price-controlled artificial attempts to preserve the "cheap food" era at the expense of the farmer could easily discourage his demand for fertilisers.

In Britain the principal post-war development is still that of compound fertiliser granulation. It is believed that well over 50% of the compound fertilisers produced for agriculture are now granulated; an appreciable number of factories now apply this process to their total output. A general survey<sup>1</sup> has shown that this development has not been free from growing pains, the tendency for rotting of fibre sacks during storage being one of the most troublesome. The addition of alkaline fillers to reduce free acidity in the pre-granulation mixture would probably obviate this trouble entirely, but at best this method can be practised only to

a limited extent because of the legal necessity to maintain water-solubility for the phosphate content. Multi-ply paper sacks are therefore being widely used. It is fair to observe that this revolution in compounding is somewhat blindly ahead of fundamental field research. For example, there is scarcely any evidence to tell manufacturers what the optimum average size of granules should be. Two motives only seem to have directed the British development of granulation; suitability for combine drilling, and better condition for storage in the barn. Nevertheless, a paper on granulated superphosphate by Dr. Sven Nordengren, read to the newly-formed Fertiliser Society,<sup>2</sup> has shown that nutrient availability and fixation are significantly influenced by granulation; though this will apply to phosphate rather than to nitrogen or potash. Five years ago it was hoped<sup>3</sup> that British field research would compare the efficiencies of powdered and granulated compound fertilisers under exactly similar conditions, but it seems that this fundamental investigation has yet to be undertaken.

The two most significant developments in the United States are each concerned with nitrogen; the increasing use of anhydrous ammonia, and the pilot-development of a "chemical" but insoluble nitrogenous fertiliser class, "Urea-form." During 1947 over 200,000 acres of cotton and maize were fertilised with anhydrous ammonia, and 1948 reports show that American use of this fertiliser is fast expanding. It has advantages over sulphate of ammonia of being cheaper per unit of nitrogen, lighter to transport per unit, and of leaving no residual anion in the soil to set up calcium-leaching and acid-tending conditions. Mechanical problems of application seem to have been overcome surprisingly well. It is also being used as a source of nitrogen in compound fertiliser manufacture, but this is only possible in a country whose criterion for the phosphate nutrient is citrate-solubility; this use of ammonia in Britain would cause reversion of superphosphate and resultant compounds would be severely penalised by the Fertilisers and Feeding Stuffs Act of 1926. Andrews and others have recently surveyed this new development.<sup>4,5,6</sup>

"Urea-form" is not a single fertiliser, but a class of fertilisers based upon urea-formaldehyde polymerisation. While most of the work so far published has come from the U.S. Dept. of Agriculture a 1947 patent<sup>7</sup> shows that the U.S. chemical industry is also interested. Hitherto the complex nitrogen-containing molecule with its slow and steady nutrient release has been the prerogative of the so-called organics; and these fertilisers have long commanded a favoured price per unit in the intensive horticultural field. It is too soon to judge whether the new polymeric materials will offer all the advantages of fertilisers like hoof and horn or dried blood. Specific conditions of time, temperature,  $p_H$ , and urea-formaldehyde ratio are necessary if the final product is to offer a nitrogen availability suited for practical use. Within a fairly narrow range, centred on about 1.3, the molar ratio of urea to formaldehyde can be varied to provide different rates of nitrogen availability. Small-scale tests, so far mainly under glass, show that the nitrogen release in the first two or three weeks is very slow and may require supplementing with a soluble nitrogenous fertiliser, but once nitrogen release begins it is said to be excellently suited to the needs of a long-season crop. A not

unimportant property of this new fertiliser is its combination of high nutrient concentration (37% nitrogen) with good and durable physical condition. It can absorb water heavily without caking and is claimed to be an excellent conditioner for compound fertilisers when used as a 5% ingredient. A number of papers and references have been published,<sup>8,9,10</sup> but the most complete account is undoubtedly that of Clark, Yeo, and Love.<sup>11</sup> It remains to be seen whether "Urea-form" fertilisers can be produced at reasonably economic costs. The U.S.D.A. research workers have stated emphatically that continuous and relatively inexpensive production is possible, but this claim is not self-evident from pilot-scale processing methods so far described. But it cannot be doubted that the development of an insoluble nitrogen fertiliser from urea, itself producible synthetically, is an important event in nitrogenous fertiliser history.

The economic background of superphosphate manufacture has changed entirely in recent years. Where formerly this fertiliser was often regarded as a convenient vehicle for utilising surpluses of sulphuric acid arising from other manufactures, it is now increasingly clear that sulphuric acid for producing current needs of superphosphate is in precarious supply; this situation must affect both output and costs, though the costs factor is obscured in Britain by a subsidy. Attention is being given, particularly in Europe, to the use of nitric acid for treating insoluble phosphatic minerals. Volkovich and Loginova<sup>12</sup> have developed a process in Russia in which the unfavourably hygroscopic calcium nitrate is removed by crystallising out at 10° C. Nitrogenous and potassic materials can then be added to produce compound NPK fertilisers. Quanquin,<sup>13</sup> in France, has described a process in which sulphuric and nitric acids are both used; enough of the former acid is added to ensure that all or most of the calcium present is converted into sulphate and phosphate. The satisfactory condition of the final mixture of sulphate, phosphates, and nitrate is ensured by granulating, N and K materials also being added. It is reported that about 100 tons per day of high-analysis NPK fertilisers are being manufactured by this new process. So-called "nitro-phosphate" fertilisers<sup>14</sup> produced by the action of both nitric acid and nitrogen oxides upon rock phosphate, have also been described.

Fusion methods of breaking up the phosphatic complexes in rock phosphate are handicapped in Britain by the water-soluble criterion; the brief war-time experiment of "silico-phosphate" does not seem to have been followed up. But Russian tests<sup>15</sup> have shown that "thermo-phosphates" have been nearly as effective as superphosphate.

Cairns<sup>16</sup> has reported large-scale efforts in Australia to attain self-sufficiency for potash, alunite—a basic aluminium potassium sulphate—being mined from the beds of almost dry lakes in Western Australia. A roasting process renders the potash water-soluble; the calcined alunite is washed with warm unsaturated potash liquors and potassium sulphate subsequently crystallised.

Mehring has surveyed the magnesium status of American fertilisers.<sup>17</sup> In 1910 the average MgO content of a compound fertiliser was 2.28%. Thirty years later it was 2.07% but over half of this amount had been deliberately added in the form of dolomite as filler. Low-grade European

potash materials, as formerly used, carried appreciable amounts of magnesium salts. The development of the U.S. potash industry after World War I led to high-grade potash materials which carried much lower amounts of magnesium salts. Dolomite is increasingly used as both an acidity-balancing and magnesium-supplying filler. In regions where magnesium deficiencies in the past have seriously diminished cropping, compound fertilisers for potatoes and tobacco are sold with guaranteed MgO contents. In addition U.S. direct use of magnesium "limestones" has risen from 58,000 tons in 1910 to nearly  $2\frac{1}{2}$  million tons in 1946.

### Application of fertilisers

The place of fertilisers in British economy has been discussed by Ogg<sup>18</sup> at the Fertiliser Society, but this paper is best studied in the Society's publication,<sup>19</sup> which includes the valuable discussion. Ogg considered that official targets for increased farm output could be attained by increased use of fertilisers alone, and he gave estimates similar to those previously made by Crowther.<sup>20</sup> The discussion showed that a number of fertiliser scientists considered that grassland as well as arable land should receive substantially increased applications. Data given by Lewis comparing British and Dutch fertiliser practice with nitrogenous fertilisers is worth particular attention. The opinion that grassland can be casually and moderately fertilised is dangerously deep-rooted, an enormous proportion of our grassland receiving no fertilisers at all; it is difficult to reconcile this with the widely realised fact that our herds cannot now be fed liberally upon imported feeding-stuffs and must obtain more of their nutrition from grass, both grazed and preserved as hay, silage, or dried grass. It is hardly an exaggeration to say that grass, our major crop, has received least attention in the matter of fertilisers throughout the recent years of fertiliser expansion.

Another contribution of general significance was Taylor's Streatfield Memorial Lecture,<sup>21</sup> discussing the Fertiliser and Feeding Stuffs Act. The baryta method for determining potash in compound fertilisers was criticised on the grounds that potash is occluded when substantial amounts of phosphate are first removed. The inability of magnesium carbonate materials to claim "lime-value" under the Act should be relieved. Taylor, like many other British soil scientists in the past few years, pressed for the recognition of citrate-solubility as a criterion of phosphoric acid availability.

Halliday has usefully analysed and summarised many years of research data on two subjects, the use of nitrogen for cereal crops,<sup>22</sup> and the uptake of plant nutrients by various farm crops.<sup>23</sup> The former Bulletin proves that our average application of nitrogen to cereal acreage in the spring is considerably below optimum; a 2 cwt. per acre rather than 1 cwt. (of fertiliser, *e.g.*, sulphate of ammonia) habit is nationally desirable. The latter Bulletin provides a wealth of information, much of which is otherwise dispersed in the literature. Some attention is paid to nutrients other than N, P, and K. Much of the data concerned had not previously been collected and analysed statistically. The periods of nutrient uptake as well as the total amounts assimilated during crop life are discussed.

However, investigations using radio-active isotope tracers are rapidly shedding entirely new light upon this subject. Spinks and co-workers,<sup>24</sup> using  $P^{32}$  as ammonium phosphate for fertilising wheat grown under glass, have shown that fertiliser P is taken up by the plant more than soil P initially, but after the first four weeks of growth the proportion of soil P assimilated increases and very little fertiliser P is taken after the heading stage. Without the tracer method of measurement the extra P taken by a phosphate-fertilised crop would indicate a 22% recovery of the fertiliser P applied; but the tracer method has shown that actual recovery is only 15.8%, the other P used being *additional* P acquired from the soil. It is indicated, therefore, that one effect of an early phosphatic application is to enable the plant to extract more soil phosphates later in its growing period. It has also been shown that as the rate of fertiliser application is increased, the proportion of soil P in the total P assimilated tends to increase. By contrast Peech<sup>25</sup> and co-workers at Cornell have made preliminary reports that most of the calcium ( $Ca^{45}$  as tracer) absorbed by alfalfa was derived from lime applied to the top-soil of an acid soil although the lower soil levels contained large amounts of calcium. A general account of this new research method and its possibilities has been given by Sauchelli.<sup>26</sup>

From almost every part of the world plot and field tests continue to demonstrate the functions of fertilisers and to establish optimum rates and methods of application. Special mention should be made of the Long Ashton vegetable plots where horticultural crops are being investigated in much the same way that Rothamsted investigated the major farm crops. These plots have now received the same annual dressings in a range of NPK variations for 24 years; they were used for soft fruits until the early period of the last war, when they were diverted to research on potatoes, carrots, cauliflowers, etc. Long Ashton Annual Reports from 1941 onwards will provide data from these continuous tests; the most recent papers by Nicholas and Catlow<sup>27</sup> show that for potatoes and cauliflower the most serious yield-reducing deficiency is that of nitrogen. Plots which had been dressed with organic manures, *e.g.*, F.Y.M. and composts, demonstrated nitrogen deficiencies unless a nitrogenous fertiliser was also applied. Potato yields were not adversely affected where chloride sources of potash took the place of sulphate of potash. This series of plot tests should be more widely known; latterly tissue tests have been used to supplement visual and cropping assessments of the fertiliser and manure effects. At the same centre Bould and Catlow<sup>28</sup> have shown that complete NPK fertiliser treatments produce the highest yields of black currants; bulky organic manures failed to provide enough available nitrogen for maximum growth and adequate nitrogen status in the foliage was not maintained on the manured plots. Pollard and Bryan,<sup>29</sup> sampling from the same plots, have established that the ascorbic acid and sugar contents of blackcurrants fall with increasing nitrogen uptake, a result which falls into line with a large number of similar observations abroad with citrus fruits; the increased fruit yield heavily outweighs the loss of vitamin C per pound of fruit, also in agreement with overseas evidence from other fruit investigations. It is not unimportant to note that over a number of years Long Ashton investigations have

consistently failed to confirm the "Nature-and-humus" school's opinion that organic composts do not require help from fertilisers; Bould<sup>30</sup> has specially discussed the nitrogen inadequacy of composts, using perfusion, fermentation, rate of nitrification, pot and field tests to obtain his evidence.

Pinck, Allison, and Gaddy<sup>31</sup> have reported a long-term experiment comparing nitrogen added directly to the soil and nitrogen added to green manure crops subsequently dug in. Where green manuring was carried out the nitrogen release to later crops was slow; much better nitrogen recovery was obtained when the nitrogen was directly applied to the indicator crops. Better C/N ratios in the soil followed green manuring, but the direct use of nitrogen raised the C content of the soil by 24% in four years. Like composts, green manures must be regarded as inefficient releasers of nitrogen, whatever their virtues as builders of soil organic matter. It is evident that the so-called natural manuring practices are best regarded as humus-making operations with the main responsibility for plant nutrient supply devolving upon fertilisers. An overwhelming majority of critical experiments in different countries and continents refutes the anti-fertiliser philosophy and its propaganda.

Increased attention has been paid to the application of fertilisers in solution. McCollam and Fullmer<sup>32</sup> have discussed this from the point-of-view of additions to irrigation waters; and Tiedjens<sup>33</sup> has discussed the use of NPK solutions to feed horticultural crops growing in the ordinary way. Differing strengths of solutions are recommended for transplanting, starter (seed-bed), and booster (during growth) solutions. The injection of solid forms of nutrient into trees to cure deficiencies has been further studied. Roberts and Landau<sup>34</sup> have successfully injected potassium and iron sulphate tablets. Scott<sup>35</sup> has injected dry salts of minor nutrients (B, Mn, Fe, Cu, Zn) into branches, using improvements in the treated branches to assess the nutrient deficiency of the tree. On the other hand, Wallace<sup>36</sup> has reported that for a major nutrient such as magnesium, insufficient amounts of the element to remedy genuine deficiency are supplied by this method.

Two important contributions have been made to the study of manganese deficiency. Wischhusen<sup>37</sup> has discussed the manganese troubles of Florida soils, surveying this plant nutrient from 1912 to the present. Florida soils may in general be regarded as special case-histories of this deficiency; from 1938 to 1942 the consumption of manganese sulphate in Florida rose from 4,000 to 11,000 tons per annum. The remedial application recommended is from 25 to 100 lb. per acre; as in British work, foliage spraying with a dilute solution has been found both rapid and efficient. Quastel, Hewitt, and Nicholas<sup>38</sup> have shown that the use of sulphur or thiosulphates as a direct soil application increase the uptake of manganese, provided that these applications are placed rather than broadcast. This method of overcoming the soil "lock-up" of available manganese appears to be independent of changes in  $p_H$ . The experimental evidence is presented as preliminary. If further confirmed, the method will be superior to the addition of manganese salts, which tend to be inhibited in the soil by the same conditions that have already inhibited soil manganese.

A recent U.S. report<sup>39</sup> has stated that a selective hormone-type

weedkiller (2 : 4-D) can be incorporated into compound NPK fertilisers without loss of potency. Various conditions of storage preceded the field tests and the storage periods were up to 10 months. This result suggests important new developments in fertilisers for cereal and grass crops.

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### CROPS (J. B. E. Patterson, M.Sc., F.R.I.C.)

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THIS section of the Reports will follow the practice begun by previous reporters of selecting subjects on which much recent work has been done, or which are of special importance at the present time. The Agricultural

Expansion Programme calls for increased output both in acreages under cultivation and in yields per acre in regular stages up to 1952, and tillage acreages in 1949 are expected to rise to 11 million acres, of which wheat will account for 2,340,000; potatoes 1,001,100; and sugar better, 391,700. The corresponding figures for 1948 were 10,651,000 acreage, including 2,188,000 in wheat, 1,116,000 in potatoes, and 404,000 in sugar beet. E. M. Crowther<sup>1</sup> has discussed the requirements of fertilisers and shown how fertiliser placement and intelligent use based on crop requirements can be of considerable help in obtaining the increases desired.

### Grassland

The search for strains of grass species and suitable seeds mixtures to close the small gap in the winter months during which the growth of grass ceases and to fill in the summer period of demand in July–August continues, and all-the-year grazing is becoming more than a vague possibility. Two seeds mixtures suitable for long-duration leys based on cocksfoot and lucerne respectively have been suggested by W. Davies.<sup>2</sup> By proper management the former may be grazed in spring or cut for silage in May and, after resting, will provide grazing in July. A further resting in September and October with a dressing of 1–2 cwt. N per acre will give pasturage in November and December. Midwinter feeding may also be given by 6 lb. p.a. each of timothy and meadow fescue with 2 lb. white clover. Haynes and his co-workers<sup>3,4</sup> have compared the effects of continuous and rotational grazing on root-distribution, run-off, and production of protective cover. Fertilisers increase root-growth in the top 2 in. of the soil while the type of grazing does not affect root density. Both systems give good control of run-off and soil losses, but fertilised rotational grazing was found to be superior to unfertilised continuous grazing. Similar work on erosion control by Johnstone-Wallace *et al.*<sup>5</sup> supports these views and emphasises the value of clovers, lime, and fertilisers. Kentucky bluegrass with clover gave the most satisfactory type of pasture. Sprague and Myers<sup>6</sup> have found that in determining yields of this association when grown in experimental plots botanical separation gave more accurate figures for clover percentage than the use of the inclined-point quadrat.

The work on the effects of legumes on the nutrition of grasses with which they are grown in association has been continued. Roberts and Olsen<sup>7</sup> found no instances under these conditions of either legumes or grasses benefiting or suffering as compared with pure stands, and concluded that evidence for the excretion of N from root nodules was inconclusive. Support for these views was given by Myers<sup>8</sup> findings, while Roberts showed that some grasses benefited from the association only under cool nights and long cool days and under specified successful combinations. Previously, Brown and Minsell<sup>10</sup> claimed that Ladino clover with either Kentucky blue-grass or Rhode Island bent-grass gave slightly larger total yields and better distributed yields than a dressing of 28 lb. N on the grasses alone. Moser<sup>11</sup> has studied the influence of leguminous plant additions on the organic matter content and available nutrient supply of southern soils. The effect of nitrogen fertilisation on nitrogen nutrition has been investigated for legumes only by Thornton,<sup>12</sup> using a range of

fertiliser types containing  $^{15}\text{N}$ , and for mixed herbage in permanent pastures by Robinson and Pierre.<sup>13</sup>

Of individual species lucerne has received much attention. Davis<sup>14</sup> shows that the yield and stand of forage under varied climatic conditions depend upon the selection of suitable strains of cocksfoot, timothy and meadow fescue as companion species. The importance of high quality seed of large size sown at  $\frac{1}{2}$  in. depth is stressed by Erickson.<sup>15</sup> Different types of phosphatic fertilisers and their effectiveness in increasing yields and feeding value have been investigated by Alway and Nesom.<sup>16,17</sup> The relationships of cations, especially Ca, Mg, K, Na, and Mn are discussed in papers published in U.S.A. and Australia.<sup>18,19,20,21</sup> Boron receives special attention in its effect on yields—1 p.p.m. available B in soil is stated to be sufficient for normal growth of lucerne containing the normal 20 p.p.m.<sup>22</sup>—on seed and hay production,<sup>23</sup> and on the feeding value.<sup>24</sup> The differentiation of the symptoms of B deficiency and potato leaf-hopper injury is described by Colwell and Lincoln.<sup>25</sup> Both entomological and mycological damage reducing seed production and measures to deal with them are discussed by a number of authors.<sup>26,27,28,29,30,31</sup> Dexter,<sup>32</sup> and Adolph and his co-workers<sup>33</sup> agree that the yields of dry matter of lucerne cut in the morning and evening are not significantly different. Evening cuts take much longer to cure and lose significant amounts of carbohydrate in the process. Hayden,<sup>34</sup> in long-term feeding tests comparing lucerne, red-clover, and soya bean hay when fed to dairy cows with maize mash, found that the restricted diet had little effect on reproduction, milk production or utilisation of nutrients, whichever legume was fed, but that clover gave a slightly higher birth weight. He concluded that no single kind of legume roughage should be fed exclusively for long.

## Cereals

The artificial production of radio-active forms of elements commonly used in fertilisers has stimulated work on the mechanism of the uptake of plant nutrients and the stages in the plant's life when maximum demands are made. By using  $^{32}\text{P}$ , Spinks, Barber, and Mitchell<sup>35,36</sup> have studied its absorption by wheat and showed that the maximum demand is in the early stages up to heading, and that transference from leaves and stems to the head follows increasing maturity. The importance of N for wheat and the effects of deficiency and sufficiency on growth and protein content in the presence of P and K fertilisers are discussed by Lal, Malakar, and Pathak<sup>37</sup> and Davidson and Buchanan.<sup>38</sup> Caldwell<sup>39</sup> suggests methods of farming for U.S.A. conditions by which organic matter may be used as the chief source of N and the use of "commercial" N may be reduced or avoided. Systems of soil management over 25 years were compared by Greaves and Bracken,<sup>40</sup> who showed that alternate peas and wheat alone prevented loss of N and that nearly all systems increased the organic matter content of the soil. Figures were given for comparison of the effect of different systems on wheat yields and the importance for wheat yields of the seasonal distribution of rainfall rather than of its intensity is emphasised.

Different species of cereals have different responses to systems of fertiliser placement. Trials carried out over a number of years by

Weidemann<sup>41</sup> showed that wheat benefited by ploughing under of manure followed by drilling of fertiliser with seed and later top-dressing. Maize, on the other hand, prefers placement of fertiliser in side-bands and gives no response to drilling with seed. Sulphate of ammonia and superphosphate together has been found to reduce significantly the percentage of heads of wheat affected by "Take-all," when compared with other combinations of fertilisers and trace elements (Angell<sup>42</sup>). The degree of infection of roots is not altered, but fertiliser dressing can partly compensate for economic effects of established infection. Similar processes are the basis of the Chamberlain system of control of the disease in intensive barley growing,<sup>43</sup> which depends upon increasing the nitrogen available in the soil to all but the first crop by undersowing with trefoil or equal parts trefoil and Italian ryegrass (20 lb. per acre) and ploughing in after harvest. Suitable manuring in balanced treatment in moderate amounts is also claimed by Macfarlan and Grainger<sup>44</sup> as the best method of control of mildew on oats. An unusual disorder of barley in which the ears were blind was widespread in E. Anglia after the abnormal snow and cold weather in the spring of 1947. Dillon Weston, Large, and Earnshaw<sup>45</sup> concluded, after consideration of 400 crop reports and the examination of 200 samples, that the abnormal weather conditions—and not thrips or hormone weedkillers as was suggested by many—produced physiological changes.

Trace element deficiencies, notably of Mo and Mn, in oats have received attention. Fricke<sup>46</sup> found that 2 oz. sodium molybdate per acre led to normal growth of Algerian oats and gives figures for Mo content of grain and plants on control and treated plots.

Hageman *et al.*<sup>47</sup> have repeated sand culture work on the necessity of 2 p.p.m. Mn in culture solution for prevention of Grey Speck in oats. Field methods of control are discussed by Sherman and Harmer,<sup>48</sup> and MacLachlan,<sup>49,50</sup> from which it is concluded that reduction of soil  $p_H$  to below 7, application of Mn salts to the soil and spraying the crop with 2% solution of  $MnSO_4$  are effective.

### Linseed and Flax

The continuance of the need for avoiding importation of protein for stock feeding has stimulated interest in the cultivation of linseed. F. W. Burmann,<sup>51</sup> in a general paper on its production and uses, states that a high rate of germination is encouraged by subsoil moisture conditions brought about by establishment of a firm seed-bed. Yields are quoted as varying from 8–16 cwt. per acre. Thorough drying of the crop before threshing is stated to be essential. The opinion held by some that linseed growing exhausts land is contradicted by enhanced yields usually given by subsequent crops.

The need for phosphorus is discussed by H. H. Flor,<sup>52</sup> and F. M. McIsaac and W. G. McGregor.<sup>53</sup> The former finds that 20 lb. per acre ammonium phosphate affects the yield of seed without affecting the quality of oil, but germination may be reduced by heavy applications. The latter show how phosphorus alone corrected chlorotic die-back on calcareous soils.

G. E. Blackman and K. Holly<sup>54</sup> discuss the important subject of weed control. The best treatment for annual weeds in linseed is the use of not more than 2 lb. MCPA per 100 gallons per acre before the plants are 3-4 in. high. Spraying must not be done after they reach 12 in. Cuprous chloride at 10 lb. in 100 gallons per acre is recommended for use when linseed is used as a cover crop for long leys. The grasses should be well established and the linseed 4-12 in. high before treatment, which controls only a limited number of weed species.

Zinc toxicity caused by galvanised wire netting covering experimental plots on sandy loam at  $p_H$  6.0 has been described by C. R. Millikan,<sup>55</sup> who has shown that retarded growth and marked chlorosis of tops can be produced or aggravated by increasing the Zn content of the soil, and prevented by application of 1 ton  $Ca(OH)_2$  before sowing. Excess Zn affects the mobility of Fe in the tissues. Spraying chlorotic plants with aq. 0.5%  $FeSO_4$  restores the normal green colour but does not relieve the stunting.

Pests and fungoid diseases have received attention. Beet army worm can be controlled by a single prompt application by aeroplane of 5% DDT dust at 20 lb. per acre according to J. N. Roney.<sup>56</sup> F. J. Newhook<sup>57</sup> suggests improvements in the Ulster method of Muskett *et al.*<sup>58,59</sup> for detection of browning (*Polyspora lini*) and of wilt (*Fusarium lini*) in seed lines of linen flax.

The relationships between meteorological conditions, oil formation, and iodine number of linseed oil is discussed by E. P. Painter, L. L. Nesbitt, and T. E. Stoa,<sup>60</sup> who conclude from observations made in 1941 and 1942 that, besides temperature and rainfall, unknown factors influence the iodine value.

### Other oil-bearing seed crops

Blackman,<sup>61</sup> who carried out during the war a wide programme of experiments on the growing of oil-bearing seed crops in this country, states that, by suitable choice of varieties, large yields of linseed or sunflowers can be obtained and that the cultivation of poppies is possible. As has been found by a number of others, soya bean cultivation is, as yet, unsuccessful. Details of methods of cultivation and harvesting of sunflowers are given in an earlier paper.<sup>62</sup> The average oil content of 33% was obtained from a wide range of yield of 5-20 cwt. per acre seed.

If attempts were made to grow this crop on a large scale, storage problems would have to be faced. As Kiermeier<sup>63</sup> has shown, under humid conditions the husks adversely affect the seeds, causing oxidation of amino acids and proteins, and would have to be considered if the seed meal were used for feeding pigs as described by Krider *et al.*<sup>64</sup> The proper use of fertilisers is necessary for production of good crops and Russian work has shown that maturity is delayed by excess N and advanced by P and K.<sup>65</sup> The sensitivity of sunflowers to boron deficiency is used by Schuster and Stephenson<sup>66</sup> for indication of B levels in soils in a test taking 8-10 weeks. As regards poppies, little seems to have been published recently, though a full discussion of soil, fertiliser, and meteorological needs is given by Gericke<sup>67</sup> in which he shows that P is the chief requirement, but that, if the  $P_2O_5$  content of the seed rises above an optimum

figure of 2.3% the oil content is reduced. Figures are given for yields and chemical composition of the crop.

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## HORTICULTURE (O. Owen)

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### Growth-regulating substances

THERE would appear to be no signs of lack of interest in the so-called plant hormones or in the uses to which they may be put. As herbicides their range of application widens and this aspect was dealt with comprehensively in the 1947 Report. Some of the other uses to which they may be applied will be considered this year. Most of the work to be covered is concerned with fruit-setting and fruit-thinning, although there have been a number of papers on rooting.

2-Naphthoxyacetic acid is now used fairly extensively in this country to induce setting of tomato fruits and there are several proprietary preparations containing 40 to 60 p.p.m. of this agent plus a suitable wetter. It is usually recommended that the spray be applied to the flower trusses or immature fruits. It is therefore interesting that A. E. Murneek<sup>1</sup> finds that while 2-naphthoxyacetic acid at 50 p.p.m. and *p*-chlorophenoxyacetic acid at 10 p.p.m. applied in the orthodox way increase yields of tomato, when the compounds are applied over the whole plant at concentrations of 20 and 1.25 p.p.m. respectively the increases in yields are greater, and this result is ascribed to the amount of the active compounds which falls on the foliage rather than to that which falls on fruit and flower trusses. He shows that 2:5-dichlorobenzoic acid at 100 p.p.m. is ineffective, but that *o*-chlorophenoxy- and 2:4:5-trichlorophenoxypropionic acids at 50 p.p.m. and 10 p.p.m. respectively are effective. The increased yields are due mainly to increased fruit size rather than to the number of fruits produced. Applications of the compounds in aerosols were not better than applications as aqueous sprays. F. S. Howlett and P. Marth<sup>2</sup> find that indolylbutyric acid and 2-naphthoxyacetic acid separately and together as aerosols, emulsions or aqueous solutions increased yields of greenhouse tomatoes. When they were used together with *p*-chlorophenoxyacetic acid the response was even greater. They point out, however, that the fruit is liable to have poor pulp after this treatment and at one centre where the trials were carried out some of the fruit was badly ribbed which, of course,

of course, is likely to reduce its market value. R. J. Hilton<sup>3</sup> finds that parthenocarpic fruits are readily induced by treating petunia and tomato flowers with indolyl- or naphthyl-acetic acids at concentrations of 0.01 to 5.0% in lanolin pastes or 0.005 to 0.25% in aqueous sprays. Similar treatment was without effect on apple blossoms. L. J. Edgerton,<sup>4</sup> using a method he has developed for the evaluation of the effect of growth-regulating substances on petiole abscission on apple trees considers that naphthylacetic acid is more effective than its salt. In this connection it is shown that variety of apple is important in that 2:4-dichlorophenoxyacetic acid has little effect on the variety McIntosh, the methyl ester has some effect, while the acid itself and its methyl and amyl esters are efficient on Stayman and Winesap.

L. C. Luckwill<sup>5</sup> has described a neat and attractive method for evaluating the relative fructigenic activities of growth-regulating substances. Tomato ovaries are treated with known amounts of aqueous solutions of the substances to be examined and the growth of the treated ovaries measured. It is shown that the response to treatment is directly proportional to the expression ( $\log D_x - \log D_c$ ) where  $D_x$  and  $D_c$  are mean diameters of the treated and untreated ovaries respectively, at the end of six days. The method requires little in the way of apparatus and it can be carried out in a normal greenhouse although, as the author points out, additional control of temperature and humidity (and, presumably, light) would enhance the precision of the test. One interesting conclusion reported is that indolylacetic acid, which is extremely active on the basis of the standard *Avena* test is relatively inactive when applied to tomato ovaries. Obviously this method will be extremely valuable in separating those growth-regulating substances which will induce parthenocarp in tomatoes from those which will not; in addition, it will grade those substances which cause parthenocarp according to their activity. Using this method Luckwill<sup>6</sup> shows that apple seeds at certain stages of development contain a growth-regulating substance which can be extracted by boiling water. In the variety Beauty of Bath the substance appeared in large quantities 30 days after petal-fall, coincident with endosperm formation and cessation of post-blossom drop. In the final stages of fruit growth a fall in amount was observed, and this coincided with pre-harvest drop and degeneration of the endosperm. It is concluded that the growth substance originates in the endosperm and that its chief function is the control of fruit abscission.

The use of growth-regulating substances for thinning apples has received a fair amount of attention. Many of the papers reviewed emphasise the fact that different varieties are liable to react in different ways. This and the conditions of spraying will often account for what appear at first sight to be contradictory conclusions. For instance, M.B. Hoffman, F. W. Southwick, and L. J. Edgerton show that sprays of 5-15 p.p.m. of the sodium salt of 1-naphthylacetic acid applied nine days after the first day of full bloom effected little thinning of the varieties, Wealthy and Rome Beauty, but caused appreciable thinning of MacIntosh and Delicious. Sprays 12 to 18 days after first day of full bloom had little effect on Rome Beauty, but had some effect on the other three varieties. That there is a "carry-over" in the effect of this type of treatment is

shown by M. B. Hoffman,<sup>8</sup> who observed that the quantity of bloom on Wealthy apples in one year was closely related to the degree of thinning effected the previous year by 3 : 5-dinitro-*o*-cresol or its sodium salt. He concludes that regular thinning makes possible annual crops of marketable fruit in a variety which normally crops biennially. A similar after-effect is reported by L. R. Bryant, C. L. Vincent, and E. G. Schafer,<sup>9</sup> where 2 : 4-dichlorophenoxyacetic acid had been effectively used to kill bindweed in an apple orchard. The following year McIntosh apples were elongated and had a very open core and both the varieties, Delicious and Jonathan, exhibited abnormalities. Using a different type of compound A. L. Kenworthy<sup>10</sup> finds that a spray containing 0.2% of polyethylene polysulphide plus 0.025% of a zinc dimethyldithiocarbamate-*cyclo*-hexylamine complex with a wetter applied 10 to 14 days after full bloom reduces fruit set by 50 to 60% in apples. On peaches F. W. Southwick, L. J. Edgerton, and M. B. Hoffman<sup>11</sup> find that *o*-dinitro-*cyclo*hexylphenol and its *dicyclo*hexylamide salt and 3 : 5-dinitro-*o*-cresol and its ammonium salt gave satisfactory thinning and an increase in the mean size of fruits.

On the other side of the picture mention must be made of a few papers dealing with the use of these compounds for reducing pre-harvest drop. L. P. Batjer and A. A. Thompson<sup>12</sup> claim that 2 : 4-dichlorophenoxyacetic acid, its sodium or ammonium salt or its butyl ester are more lasting in effect than the usual sprays, such as naphthylacetic acid. C. P. Harley, H. H. Moon, and L. O. Reigembal,<sup>13</sup> on the other hand, conclude that except for the butyl ester the other three compounds are ineffective with a number of apple varieties. W. S. Stewart and E. R. Parker<sup>14</sup> show that 2-25 p.p.m. of 2 : 4-dichlorophenoxyacetic acid was as effective as 225 p.p.m. in preventing pre-harvest drop in grape fruit when applied to almost mature fruits. The higher concentration reduced yields and tended to produce abnormal fruits. That external factors have a bearing on the procedure is shown by M. B. Hoffman and L. J. Edgerton,<sup>15</sup> who report that the effectiveness of naphthylacetic acid for pre-harvest drop in McIntosh apples is reduced when soil moisture is too low. R. M. Smock and C. R. Gross<sup>16</sup> show that 10-25 p.p.m. sprays of naphthylacetic acid may increase respiration of the apples after picking and the sprayed fruit tends to soften more quickly.

There is little report on the use of these substances in promoting root formation, but P. W. Zimmermann and A. E. Hitchcock,<sup>17</sup> who have done so much pioneer work in this field publish a timely reminder that the age of the tissue largely decides whether formation of adventitious roots is possible whether a hormone is used or not.

F. Molwus<sup>18</sup> reports that the expressed juices of over 300 plants contain a substance called "blastocholine," which inhibits germination and can counteract the effect of auxin, etc.

## Vitamins

J. M. Leichsenning, L. M. Morris, D. A. Grambow, and E. G. Donelson<sup>19</sup> state that the effect of environmental factors outweigh those of fertiliser treatment in respect of the ascorbic acid content of potato tubers. This principle is confirmed by B. E. Jones,<sup>20</sup> who shows that the ascorbic acid contents of several vegetables are not significantly decreased by high

fertiliser treatment. S. A. Wittwer and A. D. Hibberd,<sup>21</sup> on the other hand, show that heavy applications of nitrogen depress the vitamin content of peaches. E. G. Hallsworth and V. M. Lewis<sup>22</sup> report that the ascorbic acid content of tomatoes is positively correlated with the vegetative vigour of the plants and the amount of light energy they receive prior to harvest. It must be assumed that plant vigour is dependent, among other things, on a correct balance and the right amount of nutrients. So that presumably the removal of fertiliser quantities from the optima will reduce desirable vigour of the plant and hence ascorbic acid content of the fruit. Hallsworth and Lewis<sup>22</sup> also find that environment is more important than variety in this connection, but that variety is important is shown by A. F. Yeager and H. J. Purinton<sup>23</sup> who, by crossing *Lycopersicon peruvianum* with a commercial tomato variety obtained a vigorous plant which back-crossed with the commercial variety eventually yielded plants with fruits of an ascorbic acid content of 25–70 mg. per 100 g. compared with the mean value of 15 mg. per 100 g. of the standard varieties. N. W. Jones and E. R. Parker<sup>24</sup> show that ascorbic acid and nitrogen contents of navel orange juice are negatively correlated and that fertiliser treatment which affects the nitrogen in the juice also affects the ascorbic acid content. The effect of the addition of copper to a greenhouse soil on the composition of a variety of crops is described by R. E. Lucas.<sup>25</sup> The ascorbic acid contents of barley, oats and autumn spinach were increased, but those of spring spinach and tomato fruit were decreased. The carotene contents of wheat, spinach, barley, carrots and oats were increased.

### Mineral deficiencies

Among the trace elements zinc continues to attract considerable attention. E. B. Early<sup>26</sup> shows that one variety of soya bean tolerates eight to twelve times as much as another. In general, varieties resistant to zinc were the larger seeded and early maturing ones. W. A. Roach<sup>27</sup> has reported some of the spectacular results he has obtained by correcting deficiencies in potatoes. In South Kent an untreated yield of 14 tons per acre was increased to 17.75 tons by spraying with 2.5 lb. per acre of manganese sulphate, to 16.65 tons with 2.5 oz. of zinc sulphate and to 19.35 tons by spraying with both salts. D. Mulder<sup>28</sup> describes the effects of zinc deficiency in Golden Delicious apples. Leaves show yellow spots and serrated edges and may be reduced to a fifth of the normal size. "Rosettes" and "witches' brooms" are found in the branches. Correction is effected by zinc sulphate and the deficiency is attributed to fixation of zinc by soil phosphates. Other varieties and also some cherry and pear trees are susceptible. A paper by C. R. Milikan<sup>29</sup> deals with soil toxic levels of zinc in flax. Stunting may occur with or without chlorosis. In the field correction is effected by a dressing of lime. The concentration of iron is higher in chlorotic than in non-chlorotic leaves. In this type of work it is always difficult and often impossible to suggest limits of concentrations at which deficiency or toxicity symptoms will appear. It is therefore refreshing to find that H. S. Reed and J. Dufrenoy<sup>30</sup> suggest that the zinc content of pea seeds should be 0.002 p.p.m. for normal growth and that to give a 30% yield of tops and roots of sunflower

and of tops and roots of radishes respectively it is necessary that the nutrient solution should contain 0.06, 0.05, 0.045, and 0.033 p.p.m. of boron. C. E. Scott<sup>31</sup> describes various deficiencies in fruit trees which, except in the case of cherry and walnut trees, are usually corrected by spraying. Of a number of ferric salts tested by G. H. Starr<sup>32</sup> to correct chlorosis in cottonwood trees by injection the phosphate is most effective. Ferrous salts were of no value. M. Drake, D. H. Sieling, and G. D. Scarseth<sup>33</sup> recommend that the calcium : boron ratio in plant ash be used as guide to boron deficiency; normal Turkish tobacco plants have a ratio less than 1340 : 1. When the ratio rises to above 1500 : 1 boron deficiency is likely to occur. C. E. Schuster and R. E. Stephenson<sup>34</sup> demonstrate the value of the sunflower as an indicator of boron deficiency. H. E. Dregne and W. L. Powers<sup>35</sup> adduce data to suggest that boron extracted from soil by boiling water is a good measure of its availability. K. C. Berber and E. Truog<sup>36</sup> support this view and conclude that of the total boron in soil as measured after fusion with sodium carbonate only about 5% is available. Magnesium deficiency in glasshouse tomatoes has been of increasing importance in this country during recent years. O. Owen<sup>37</sup> described the symptoms. Later,<sup>38</sup> he reported that spraying with 2% Epsom salts solution corrected the disorder and was markedly superior to soil applications. D. J. D. Nicholas<sup>39</sup> has reported results of several years' work on this problem. He confirms Owen's findings and suggests that the spraying may be combined with a Shirlan A.G. which is used for controlling tomato leafmould. While this economy of labour is desirable it is unlikely that Epsom salts can be mixed with impunity with other sprays used on tomatoes and it is within the reporter's knowledge that many cases of injury have occurred when the magnesium sulphate spray has been applied to plants with or immediately after an oil emulsion spray. H. Hill and F. B. Johnstown<sup>40</sup> report that applications of Epsom salts to the soil may not give a complete response for two or three years in Quebec orchards, and four sprays of 2% solution are recommended as a temporary control measure.

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## THE APPLICATION OF INSECTICIDES AND FUNGICIDES (H. Martin)

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THE discovery of non-poisonous stable and highly potent insecticides, of which DDT is the best known, has made feasible the localised elimination of insect-borne diseases of man and stock. The limiting factor is the economic application of the insecticide to wide areas of bush, swamp or jungle. Established methods, with which this review is mainly concerned, help but little in the solution of this problem, for, with only poisonous and dangerous insecticides available, they had as their object a precise and limited distribution. Moreover, with the older pest control materials such as lead arsenate or lime sulphur, the margin of safety between the concentration giving effective control and that liable to cause damage to the treated plant was so small that fool-proof methods of controlling the amount remaining upon the treated plant were required.

### Hydraulic spraying

This object was achieved by using water to carry the active spray material. The amount retained is thereby automatically controlled by the interfacial tensions, the excess fluid running off.<sup>1</sup> Water-insoluble materials are applied as emulsions or suspensions, a preferential retention of the non-aqueous phase being avoided by a suitable choice of emulsifier or protective colloid. The proposed use of quick-breaking emulsions<sup>2</sup> or of oil-flocculated suspensions<sup>3,4</sup> to reduce loss in run-off has not been widely adopted because of the non-uniformity of the spray residue and the loss of the safety factor.

Control over the distribution of the spray is obtained by the use of high pressures and specially designed nozzles. The earlier work of Davies and Snythe-Holmwood<sup>5</sup> on the performance of spray nozzles has been completed by Kearns,<sup>6</sup> who has proposed a standardised design. With a fixed depth of swirl-chamber (about  $\frac{1}{4}$  in.) the droplet size distribution and the angle of the spray cone are governed by the relative areas of the central and side ports of the swirl-plate, the larger the central hole the coarser is the spray and the narrower the spray cone. For top fruit spraying, a swirl-plate of six-side holes, each of  $\frac{7}{32}$  in., and one central hole of  $\frac{1}{8}$  in., is widely used, and gives an effective range of some 15 ft. when operated at pressure of 400 lb./sq. in. By suitable spacing of two or more nozzles on a spray broom a greater throw and wider sweep of spray is obtained, but the greatest volume of spray which one operator can manage efficiently is 9 gal. per min., an amount given by three nozzles with  $\frac{6}{64}$  in. disc apertures. With this spray broom accurate spraying is possible in breezes up to 10 m.p.h. (Beaufort scale 3). Spraying in stronger breezes is avoided because of the danger of drifting spray to previously sprayed and dried surfaces increasing the deposit beyond the normal "run-off" amount. As top-fruit takes a thousand or more gallons of spray per acre and as the critical time for spraying may be as brief as ten days, the acreage which can be covered by one spray machine with a driver and two men is 20 to 40 acres. Spraying is therefore costly and even with high value crops, cheaper methods, using less labour, are being examined. One tendency is towards so-called automatic spraying, long used for row crops and hops, in which the spray broom is replaced by a spray-boom with a fixed array of nozzles. The spray machine is then drawn slowly between the tree rows delivering up to 40 gal. per minute. Savings of 30% spray, 73% man-hours, and 45% time have been reported,<sup>7</sup> but there is little critical data on relative efficiency in pest control. The successful use of automatic sprayers may require a drastic modification of the present planning of fruit plantations to a system with the trees grown as hedges.<sup>8</sup> Another tendency is towards spray materials with which the risk of damage through over application is low enough to warrant departure from conventional spraying. The safe insecticide is already available, but safe protective fungicides are still experimental, though the argument that lime sulphur is so cheap that the economic prospects of a substitute are meagre loses weight if the more expensive substitute is cheaper to apply.

### Dusting

Under conditions of short water-supply, or when the terrain is unsuitable for heavy water-carrying machinery, dusts, in which the active insecticide is diluted with an inert powder, have long been used. The dry mixture is dispersed in a strong air current produced by power-driven fan or turbine blower. The dust should flow freely, should disperse easily and should adhere well to the treated surfaces, but little fundamental is known of the factors governing these properties. In dispersion and adhesion the electrification of the particles may be important, and this has been studied by Wilson who, in his latest paper,<sup>9</sup> concludes that the electrostatic properties of a powder are controlled by two general factors :

(1) mineralogical characteristics affecting particle size, (2) lattice structural arrangements. Negative charges were developed with acidic materials such as silicates exposing  $\text{SiO}_2$  tetrahedral structures on fracture; positive charges appeared on alkaline material or on silicates exposing alkaline cations or OH structural groups on fracture. The direct electrification of dusts on emergence from the duster is attempted in a novel French machine.<sup>10</sup>

Practical experience has shown that the biological efficiency of dusts is much lower than that of sprays; 6–8 dustings are required to protect potatoes from blight to the degree obtained with two sprayings. This difference is due mainly to the poorer tenacity of the dust, and trials have been made with oil-impregnated dusts and with the admixture of liquid droplets with the dust to improve its adherence. Several experimental “liquidusters” have been partly described (see <sup>11</sup>). Potts<sup>12</sup> found the mere mixing of dust and oil particles ineffective, but by atomising the liquid by the air-dust stream, oil-coated solid particles were obtained which adhered to foliage better than the uncoated dust.

For the application of dusts to seedling crops for the control of flea beetle, Staniland and Mayor<sup>13</sup> devised a simple home-made machine using a square wheel to jolt the dust through hessian containers.

### Mist spraying

For domestic use the “atomiser” principle of the scent-spray has long been used to disperse kerosene solutions of insecticides. This principle was adopted for spraying DDT solutions in petroleum oils from aeroplanes when air speed alone is sufficient to shatter the solution into droplets which are dispersed in the slipstream. Gunn<sup>14</sup> concluded that, by laying overlapping swathes, a sufficiently uniform deposit can be obtained, given a steady wind velocity. The helicopter<sup>15</sup> would probably permit a more controllable distribution because of the down draught of the rotor blade, but this advantage and those of lower air speed and height are offset by the more restricted range and lower load of the helicopter.

The war demand for smoke screens exceeded the supply of smoke-forming chemicals, and appliances were devised for making fogs from petroleum oil. Tests of these machines, *e.g.*, the Hochberg-La Mer and Todd generators, soon followed for the production of insecticidal fogs.<sup>16</sup> For screening purposes, the best particle size is  $\frac{1}{2}$ –1  $\mu$  but, to obtain an effective control over distribution, a particle diameter of 10–50  $\mu$  would seem necessary. Moreover, the efficiency of the mist against flying insects increases rapidly with particle size,<sup>17,18</sup> an increase associated with the poorer “pick-up” of the finer droplets by the insect wings.<sup>19</sup> Similarly it has been found that liquid or solid particles when below a certain diameter of the order of 1  $\mu$  do not make contact with solid surfaces to which they approach. The prospects of the open air use of the fog generator for the application of insecticides do not therefore seem promising.

A novel method of producing a fine spray with low power consumption is by adding a frothing agent to the spray which is passed through a baffled “foam-chamber” before introduction in a low-pressure stream of air.<sup>20</sup> This method recalls a grower’s suggestion that strawberries could

be rid of aphides by applying nicotine in the gaseous phase of a foam, but this method is unlikely to replace drag-sheet fumigation which, by permitting an accurate control of dose, enables a destruction of aphides without serious mortality among beneficial predatory insects.<sup>21</sup>

### Fumigation

For the treatment of closed spaces, fumigation is still the best method, being greatly extended in range and efficiency by the discovery of successful ways of generating "smokes" of DDT, BHC, azobenzene, and HETP. Pyrotechnic smoke generators are described by Bateman and Heath,<sup>32</sup> and in the United States, solutions of the insecticides in a liquidified gas have become popular for domestic and glasshouse work. This method has already been described in these reports under the heading "Aerosols," which has replaced "particulate" as a fashionable word for matter in a fine state of subdivision. The non-impaction of such fine particles on surfaces other than horizontal renders the method less effective if a persistent insecticidal deposit is required on roofs and walls. The formation of insecticide films on building materials has been investigated at the D.S.I.R. Pest Infestation Laboratory,<sup>23</sup> where a pre-treatment of porous surfaces has been found advantageous.

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## CONTROL OF PLANT NEMATODES (B. G. Peters, Ph.D., M.Sc.)

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It is unfortunate that such modern insecticides as DDT<sup>1</sup> and benzene hexachloride are not effective against plant eelworms. Thus, rates up to 214 lb. per acre of 0.5% gammexane was without effect on *Heterodera marioni* in Rhodesian tobacco soils,<sup>2</sup> and Clayton and Ellis<sup>3</sup> found no control of the same eelworm in U.S.A. at rates (up to 675 lb. per acre) highly toxic to plants.

The older nematocides continue to be tried. Calcium cyanamide, with urea, was said to control *H. marioni* in Carolina,<sup>4</sup> but, in Rhodesia, Thompson<sup>5</sup> found no effect from calcium cyanamide at 1000 lb. per acre. Chloropicrin is recommended by Christie (in Doolittle<sup>6</sup>) for glasshouses and small plots which can be water-sealed, and also by Massey,<sup>7</sup> Naude,<sup>8</sup> and Taylor and McBeth.<sup>9</sup> Stark and Lear<sup>10</sup> found it slow in penetrating root galls. All these relate to *H. marioni*, but it has also been effectively used against cystic species of *Heterodera*, viz., *H. schachtii*<sup>11</sup> and *H. rostochiensis*<sup>12</sup> and (before transplanting) against the citrus eelworm.<sup>13</sup> Chloropicrin has also been the subject of useful studies on diffusion through soil by Schmidt,<sup>14</sup> and on adsorption by soil and other edaphic factors by Stark<sup>15</sup>; these studies are fundamental to soil fumigation generally.

The majority of newer nematocides are fairly simple halogenated hydrocarbons; useful summaries of the soil fumigants are given by Christie,<sup>16,17</sup> Newhall,<sup>18</sup> and Lange.<sup>19</sup> As a soil fumigant, ethylene chlorobromide was found by Christie<sup>17</sup> to give useful control of *H. marioni*, whereas with potted perennials Tarjan<sup>20</sup> found it of little use at doses not phytotoxic (below 0.25 c.c. per pot). Ethylene dichloride has been found of some use against *Heterodera schachtii*<sup>11</sup> and citrus eelworm.<sup>13</sup> Propylene dichloride has been used by Lear<sup>21</sup> as a 90% diluent for ethylene dibromide and is reported also<sup>12</sup> as a solvent for methyl bromide, but by itself is a poor nematocide.<sup>19</sup> As a gas methyl bromide is unsuitable for soil fumigation on a large scale unless in solution; but Grant<sup>22</sup> recommends farmers to use it for fumigating onion seed (against *Anguillulina dipsaci*), to which Moulds<sup>23</sup> replies that its haphazard use is dangerous. It has been used to fumigate seed potatoes (*H. rostochiensis*) but McCubbin<sup>24</sup> states it is liable to damage them.

Of the saturated hydrocarbon derivatives, however, the best soil fumigant to date is ethylene dibromide. Used in concentrations of 5% to 20% (v/v) in solvent naphtha,<sup>16</sup> it has been reported as successful against *H. marioni*;<sup>6,7,10,21,25</sup> at rates up to about 70 gall. per acre of the 10% solution. Thorne and Jensen<sup>26</sup> obtained increased beet yields from a 15% solution used at 400 and 200 lb. per acre, against *H. schachtii*, but eelworms multiplied greatly on the larger beets produced. Using *H. rostochiensis* in a pot test, Schmitt<sup>27</sup> reported eradication from using a 10% solution at the rate of 76 gall. per acre. *Ditylenchus destructor*<sup>28</sup> and *Pratylenchus pratensis*<sup>29</sup> have also been partially controlled. Although not considered a fungicide, its success in controlling cotton wilt<sup>30</sup> may

be due to its killing nematodes which damage the cotton roots and so admit the fungus.

D-D mixture and other control agents are held over for consideration next year.

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## ANALYSIS OF AGRICULTURAL AND HORTICULTURAL MATERIALS (J. H. Hamence)

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### Fertilisers

RELATIVELY few papers have appeared during the period under review on the analysis of fertilisers.

The increasing use of ammonium nitrate in fertilisers has led Prince<sup>1</sup> to record results of collaborative work to determine ammonium nitrate in mixed fertilisers using the Kjeldahl, Devarda, etc., methods. The Jodlbauer or modified Kjeldahl method was found to be unsatisfactory in presence of chlorides, thus confirming previous workers in this field.<sup>2</sup>

Jacob *et al.*<sup>3</sup> have made an exhaustive study of the solubility in neutral ammonium citrate and 2% citric acid of phosphoric acid in phosphatic

fertilisers containing  $\alpha$ -phosphates, *i.e.*, products obtained by heating natural phosphates to a high temperature in the presence of silica.

As in the case of other phosphatic materials 2% citric acid extracts more phosphoric acid than neutral ammonium citrate.

The solubilities are not increased by grinding finer than 200 mesh. The presence of fluorine has a marked influence on solubility and increase of solubility occurs as the fluorine content diminishes. Partly defluorinated phosphate has a high solubility when fluorine content is less than 0.5%, and the solubility in citrate is only slightly less than the solubility in citric acid.

The results are important in view of the increasing use of defluorinated phosphate in America.

A report on collaborative work on the determination of potash in fertilisers is given by Ford.<sup>4</sup> This work was carried out on the official American method, and it showed that sodium acetate could be employed instead of sodium hydroxide in the initial ashing process and that in the final chloroplatinate process the strength of alcohol was not important provided it was greater than 85%.

In order to avoid errors due to oxidation which occur when some types of fertilisers are dried at 100° C. for five hours in order to determine the moisture content, Hardesty *et al.*<sup>5</sup> have described a method for determining moisture in fertilisers by drawing air over the sample at 60° C. for two hours.

This method is compared with the results given by drying at 98–100° C. for five hours and vacuum-drying in a paper by Ross and Love.<sup>6</sup> These workers find that for materials containing occluded moisture the air-flow method gives higher results than the vacuum-drying process. For other stable materials, however, the three methods give the same results.

### Feeding stuffs

Papers on the analysis of feeding stuffs have nearly all been reviews of existing methods.

Taylor<sup>7</sup> reports on collaborative work carried out to determine the crude fat in dairy feeds. Extraction with ether was found to give higher results than extraction with light petroleum, a finding which has been accepted for many years in this country.

The efficiency of mercuric oxide and copper sulphate as catalysts in the determination of protein in fish meal by the Kjeldahl process has been studied by Potts *et al.*<sup>8</sup> who report the mercuric oxide gives higher results.

A comparison of the results obtained for nitrogen in pasture grass by the Kjeldahl method and three modifications of the micro-Dumas method are described by White *et al.*<sup>9</sup> Results given by the standard micro-Dumas technique were found to be low and erratic; the potassium chlorate technique in which the reduced residue is reburnt in oxygen gave reproducible results in good agreement with those obtained by the Kjeldahl method.

Lewis<sup>10</sup> has described a modification of the Norman-Jenkins method

for the determination of cellulose in agricultural residues which requires only one-half to one-third of the time.

The determination of cobalt in grass and hay has been studied by Seekles *et al.*<sup>11</sup> who employed the nitroso-R-salt method which was used to determine cobalt in pasture grass and hay from areas in which cobalt deficiency in cattle and goats occurs.

A new procedure for the determination of selenium in horticultural materials has been developed by McNulty.<sup>12</sup> After destruction of the organic matter by sulphuric, nitric, and perchloric acids in the presence of a vanadium catalyst the selenium is distilled off with hydrobromic acid into hydrazine sulphate solution. The resulting solution is treated with uric acid and formic acid and boiled until the bromine is reduced. The solution is neutralised with 45% sodium hydroxide to phenol phthalein, acidified with sulphuric acid and titrated with thiosulphate after the addition of potassium iodide and starch.

## Soils

Hurwitz and Batchelor<sup>13</sup> have developed a colorimetric method for the determination of small amounts of potassium in soil extracts by the chloroplatinate method. After separation of the potassium as the chloroplatinate the precipitate is treated with a potassium chloride-hydrochloric acid buffer solution of  $p_H$  1.5 and potassium iodide. After two hours the solution is filtered and the colour of the filtrate compared with standards.

Causes of variation in the carbon content of soils determined by the Walkley-Black method employing sulphuric acid and potassium bichromate have been studied by Walkley.<sup>14</sup> The inorganic constituents of the soil have little effect on the results; the principal variations in the results obtained by the method being due to differences in the nature of the organic matter itself.

Graham<sup>15</sup> also determined soil organic matter by treating the soil with sulphuric acid and potassium bichromate. After dilution, the solution is allowed to stand for five hours and the colour of the supernatant determined.

The use of carmine as an indicator in the colorimetric determination of boron is described by Evans and McHargue,<sup>16</sup> and Bertrand<sup>17</sup> reports on a spectrophotometric method for the determination of lithium.

For the rapid determination of soil nutrients Wolf and Ichisaka<sup>18</sup> recommend extraction of the dried soil with sodium acetate-acetic acid mixture of  $p_H$  4.8 and describe rapid colorimetric tests for N, P, K, and CaO.

The measurement of the oxidation-reduction potentials of soils is discussed by Quispel,<sup>19</sup> who finds that satisfactory determinations can only be made in the field or on samples transported with the minimum of disturbance. The author describes suitable sampling equipment.

Other methods of collecting undisturbed soil samples are put forward by Crombie<sup>20</sup> and Lutz.<sup>21</sup>

The electrical conductivity of soil solutions or soil extracts has been found by Wilcox<sup>22</sup> to give a measure of salinity in routine soil work.

Two different pieces of apparatus for obtaining soil extracts by leaching or percolation in closed system have been described by Black<sup>23</sup> and Lees.<sup>24</sup>

### Growth regulating substances and insecticides

Swanson<sup>25</sup> has determined the herbicidal effectiveness of plant growth-regulating substances in oil solution by studying the growth of kidney bean and soya bean plants after the leaves have been specially treated with standard amounts of material.

In view of the fact that apple varieties differ in the extent to which the falling of their fruit can be prevented by sprays containing 2:4-dichlorophenoxyacetic acid, Harley *et al.*<sup>26</sup> have devised a biological method to evaluate varietal response.

Methods for the determination of DDT residues on agricultural produce have been reviewed by Carter,<sup>27</sup> who formed the opinion that reliable results may be obtained by total and labile chlorine determinations if other halogenated compounds are absent. Colorimetric methods give results substantially in agreement with those given by chlorine determinations provided that coloured extracts can be decolorised before applying the tests.

The importance of using isopropyl alcohol free from water in the total chlorine method of estimating DDT is stressed by Fleck.<sup>28</sup>

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## ANIMAL NUTRITION (W. Godden)

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IN view of the increase in the practice of artificial insemination in dairy herds Branton *et al.*<sup>1</sup> have investigated the feeding standards for bulls kept for this purpose. They used rations in which 60% of the total digestible nutrients was provided by mixed hay and 40% by concentrate mixtures containing 12.38, 15.37, and 18.48% of protein respectively and fed the rations at three levels, *i.e.*, 100, 120, and 140% of the maintenance requirements of dry cows of equivalent weight. On the basis of semen characteristics, fertility of the semen used for artificial insemination, and changes in body weight, they found that such relatively wide ranges of total digestible nutrients can be given to bulls over a period of at least 90 days without any detriment. A concentrate mixture, containing 12% of protein, when mixed with hay containing 8.9% protein was also adequate. A practical feeding schedule would be 1 lb. of such hay plus 0.4–0.5 lb. of concentrates daily per 100 lb. live weight. Wallace,<sup>2</sup> in a very comprehensive examination of the effect of plane of nutrition of the ewe on the growth of lambs before and after birth found that the dietary level of the ewe during the latter part of pregnancy (last six weeks) had a profound influence upon the birthweight of her offspring and its vigour, on her milk yield and hence on the subsequent growth of the lamb(s). He was unable to relate this to any individual dietary constituent. It remains to be seen by further investigation whether the period of six weeks before lambing for the care of dietary regime could be shortened with equal effects. Krider<sup>3</sup> has found that the following nutritional requirements should be fulfilled for sows during pregnancy and lactation. The ration should contain 14–16% of protein if on dry feed or 11–14% if the sows are at pasture; 0.22–0.45% of calcium and 0.19–0.37% of phosphorus according to the stage in lactation. Vitamin requirements per 100 lb. live weight per day are 13,000 U.S.P. units of vitamin A for pregnant sows and gilts, to be doubled during lactation; 250 U.S.P. units of vitamin D. Addition of lucerne meal or “distillers’ solubles” supplied essential B vitamins and lucerne meal appeared to supply in addition a factor or factors essential for the survival and growth of suckling pigs. The addition of 3–6% of “sardine condensed fish solubles” to rations, commonly accepted as satisfactory, improved weaning results.

Vitamin requirements of poultry have been studied by Hegsted and Perry,<sup>4</sup> who give the approximate requirements for growth of ducklings as 400  $\mu$ g. of riboflavin and 1100  $\mu$ g. of pantothenic acid per 100 g. of food. For maintenance the figures are 90 and 100  $\mu$ g. respectively. Bolton<sup>5</sup> gives the requirements of White Wyandotte chicks for riboflavin as 350  $\mu$ g. for optimal food consumption, 300–350  $\mu$ g. for optimal growth and 360  $\mu$ g. per 100 g. of food for prevention of curled toe paralysis. The amounts of this vitamin in the liver, kidneys, heart, and leg- and back-muscles were maximum at an intake of 400  $\mu$ g. per 100 g. of food and this value is probably the best criterion of minimum requirement. Gillis *et al.*<sup>6</sup> found that hens should receive 650–1000  $\mu$ g. of pantothenic

acid per 100 g. of food for proper hatchability of their eggs. Embryonic mortality due to deficiency was confined to the last 2-3 days of the incubation period. Egg production and maintenance of the hen's weight were not, however, affected over a 10-week's period with an intake level of only 150  $\mu$ g. per 100 g. of food. The use of fish solubles in various forms has attracted attention. German *et al.*<sup>7</sup> found that the addition of 5% of condensed fish solubles to a basal ration, adequate in riboflavin and containing soya bean oil meal and maize, raised the rate of growth of turkey poults by 15%, whereas the addition of a similar amount of dried skimmed milk lowered the growth-rate. The work of Mishler *et al.*<sup>8</sup> indicates a definite supplementary action between fish solubles and soya bean meal for chicks, particularly the males. Even with 1.5% dry weight of fish solubles the ration still showed a deficiency of methionine and possibly also of nicotinic and pantothenic acids. Robblee *et al.*<sup>9</sup> have examined the properties of chick growth factor in condensed fish solubles and shown that it is soluble in water; it can be dialysed through a cellophane membrane, is soluble in 70%, but less so in stronger, methanol or ethanol, is destroyed by autoclaving for 20 minutes at a pressure of 15 lb./sq. in. with 0.1 N-HCl or NaOH. The factor is thought to differ from that, also required by chicks, which is present in cow manure.

Gillis *et al.*<sup>10</sup> have compared the values of different types of phosphatic supplements for chicks and found that orthophosphates and mono-, di-, and tri-calcium phosphates are slightly more available than is steamed bone meal. Defluorinated superphosphate or phosphate rock products and also calcium hydrogen pyrophosphate are good sources of phosphorus. Vitreous calcium and sodium metaphosphates, potassium metaphosphate,  $\beta$ - and  $\gamma$ -calcium metaphosphate, and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -calcium pyrophosphates and crude calcium phytate are but slightly available or unavailable.

Considerable interest has attached to the question of canine hysteria and its onset following the consumption of "agenised" flour in the ration. Newell *et al.*<sup>11</sup> showed that fits were produced in dogs fed on flour bleached with nitrogen trichloride or a mixture of nitrogen trichloride and benzol-peroxide, but not with the latter alone or various other "agenising" agents. Fractionation showed that the toxicity was associated with the protein. No harmful effects were found with rats, chicks, guinea-pigs or humans. Monkeys had no fits but cats had convulsions. Mellanby<sup>12</sup> traced the toxic action of the agenised flour to the gluten fraction of the dough and found that, whilst both its gliadin and glutelin fractions produced a typical hysteria syndrome when fed to dogs, the glutelin was less toxic than the gliadin. Ferrets developed typical symptoms of hysteria when fed on agenised flour or its gluten fraction. Moran<sup>13</sup> found that nitrogen trichloride reacted with other proteins, *e.g.*, casein and zein, producing substances which caused hysteria and from the same laboratory (Bentley *et al.*)<sup>14</sup> later work has been reported, which seems to indicate that it is the methionine portion of the protein molecule which is involved in the production of the toxic substance(s) by the nitrogen trichloride. Parry,<sup>15</sup> whilst supporting the above findings as to the effect of agenised flour, points out that in such studies it should be remembered that numerous virus, parasitic, and spontaneous disorders in the dog may give rise to similar symptoms.

Nordfelt and Hyden<sup>16</sup> have tested the effect of the addition of 0.5, 1.0, and 2.0 g. respectively of iodinated casein per 200 lb. live-weight daily to the rations of fattening pigs of 60–200 lb. live-weight and found that, when the animals were fed to appetite, they showed higher growth rates, but a higher food consumption per lb. of live-weight increase, rising roughly in proportion to the amount of iodinated casein fed. They consider that 0.5 g. of iodinated casein per 200 lb. live-weight would produce economic gains with an estimated increase of 10–15% in the growth rate and without additional food consumption per unit of gain or any deleterious effect on health. Braude<sup>17</sup> also found a greater and more efficient gain in pigs having iodinated casein and stilboestrol added to their food during the fattening period. Using levels of only 0.15–0.3 g. of thyro-protein per 200 lb. live-weight daily Vander Noot *et al.*<sup>18</sup> found no influence on rate of gain or economy of food consumption. They record, however, that, the addition of 0.25% of thiouracil to the ration of pigs, after they have reached their desired skeletal development, improved the economy of food consumption. McMillen *et al.*<sup>19</sup> also found that the addition of 0.1% of thiouracil to the rations of fattening pigs gave an increase in the economy of food consumption, but a slightly lower rate of live-weight increase. They report that the pigs became increasingly sluggish during the 41 days feeding period, but found no effect on carcass quality.

As part of an investigation into the relative supplemental values of the protein in certain feeding stuffs that are commonly used to correct the protein deficiencies of the cereal grains and their by-products Woodman and Evans<sup>20</sup> determined the digestibility by pigs of a number of such protein-rich foods. Of these materials whale-meat meal had the highest crude protein and the lowest ash, calcium and chlorine contents. On the basis of the digestibilities of their total organic matter (about 90%) there was little to distinguish between whale-meat meal, white fish meal, feeding meat meal, extracted ground-nut meal, and dried yeast. The value for extracted feeding meat meal was 83.9 and for bean meal 78.7%. The digestion coefficients of the crude protein ranged from 80.4% in bean meal to 95.4% in white fish meal. It should be noted that almost the whole of the crude protein is "true" protein in whale-meat meal, but that, if this material is added to a cereal type of ration for young pigs, it is essential to include a mineral supplement (*e.g.*, 2% of a mixture of three parts by weight of ground chalk and one part of common salt). Under such conditions 7.25% of the whale-meat meal could replace the 10% of white fish meal commonly included in such rations. Extracted decorticated ground-nut meal had a slightly higher content of digestible true protein than white fish meal, while dried yeast came between white fish meal and bean meal in this respect, but required supplementing with a mineral mixture similar to that recommended for whale-meat meal. These two workers<sup>21</sup> have made a further investigation of the value of dried grass meal for growing and fattening pigs and report that grass meal could form 33% of a ration, fed as a thick slop with water to pigs of 45–50 lb. live-weight. Under such conditions grass meal contributed its full value, calculated from its content of total digestible nutrients, towards maintenance and live-weight increase up to a live-weight of

150 lb. Beyond this it was found desirable to reduce its amount to 25% of the ration.

During the war Fingerling *et al.*<sup>22</sup> investigated the nutritive value of various foodstuffs by feeding them to different classes of stock maintained in respiration calorimeters. The results have now reached this country. Trials with maize meal and with oatmeal when fed to pigs gave the following respective digestibility coefficients: crude protein 87.5, 85.9; true protein 87.1, 83.7; fat 83.0, 92.9; nitrogen-free extractives 96.3, 74.0; crude fibre 89.4, 17.5%. On a dry matter basis the mean productive energies per 100 g. were 301.4 and 255.0 cal. and the starch equivalents 88.4 and 74.7. The data for cocoa-shells when fed to bullocks were: digestibility coefficients of organic matter 45.4, crude protein 24.4; true protein 1.9; fat 87.6; nitrogen-free extractives 58.8 and crude fibre 7.0%. The mean starch equivalent on a dry matter basis was 36.8 and the availability coefficient 87.1%. Artichoke tubers gave the following digestibility coefficients for bullocks and pigs respectively: organic matter 82.9, 87.1; crude protein 31.9, 46.2; true protein 19.7, 12.9; fat -ve, -ve, nitrogen-free extractives 92.3, 94.9; crude fibre 31.3, 70.7%. The mean starch equivalents were 67.1 and 47.8, and the availability coefficients 88.5 and 58.1%. The differences in the starch equivalents and availabilities are considered to be due to the high content of levulose in the tubers.

Ferguson<sup>23</sup> draws attention to the fact that in two years' trials top-dressings of 2 cwt. of sulphate of ammonia or 3 cwt. of nitrochalk per acre when applied to third-year ley and old meadow grass respectively 8-13 days before cutting, increased the crude protein by 2.0% and the true protein by 1.2%, on a dry matter basis, in these hays. The digestibilities of these two constituents in the hays by sheep were also considerably higher as a result of the top-dressings. Further trials with urea as a protein-sparing material have shown<sup>24</sup> that growing lambs can utilise urea as well as pre-formed protein if the protein content of the ration does not rise above 12% and only 50% of the total nitrogen comes from urea and 25% from pre-formed protein. Also<sup>25</sup> that, when fed along with cotton seed meal, so that each supplied 50% of the total N, to yearling and two-year-old steers, the effect of urea in promoting nitrogen storage was as good as that of cotton seed meal.

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## VETERINARY MEDICINES (A. N. Worden)

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### Sulphonamides

SINCE the war there has appeared an extensive literature upon the applications of sulphonamide therapy in veterinary practice, and from the clinical standpoint this has been usefully reviewed by Scheidy.<sup>1</sup> The advantages over other sulphonamides of sulphamerazine and sulphamethazine in the production of higher and more stable blood concentrations in various species has been demonstrated by several workers.<sup>2,3,4,5,6,7</sup> Species differences in the acetylation and de-acetylation of the *p*-amino-group of sulphonamides in animal tissues have been clearly demonstrated by the use of sulphamezathine and its *N*<sup>4</sup>-acetyl derivative.<sup>8</sup> Caecal coccidiosis in poultry can be controlled by treatment with sulphadiazine administered as the sodium salt in the drinking water.<sup>9</sup> Sulphamezathine also is of considerable value in this condition, but has certain undesirable side effects, including a lengthened blood-clotting time which may be prevented by administration of vitamin K: sulphapyrazine, however, is even more effective than sulphamezathine yet does not possess these undesirable effects.<sup>10</sup> Sulphamezathine and probably sulphapyrazine are likely to prove effective in controlling outbreaks of hepatic coccidiosis in rabbits.<sup>11</sup> Some of the toxic effects otherwise attributed to coccidiostatic sulphonamides in chickens appear to be due to other factors,<sup>12</sup> but precautions regarding the practical utilisation of such methods are nevertheless essential.<sup>13</sup> Di(*p*-aminophenyl) sulphone has been used with success in the treatment of four outbreaks of bovine coccidiosis associated with *Eimeria zurnii*.<sup>14</sup> Intravenous dosage with sodium sulphapyridine has been reported as a marked advance in the treatment of "foot rot" or "foul of the foot" in cattle—a disabling condition responsible for considerable economic loss.<sup>15,16</sup> In a controlled experiment involving 136 cattle, however, the results obtained were much less dramatic than those claimed in the field.<sup>17</sup> A careful attempt to control mastitis (associated with *Streptococcus agalactiae*) in a herd indicated that whilst initial success could be obtained in the reduction of infection, complete eradication of the organisms was achieved for a short period only. The resistance of the organism in extraneous sites

together with the retention of refractory cases, appeared to be important factors in the progress made.<sup>18</sup>

### Penicillin

Like the sulphonamides this drug is now extensively employed in veterinary practice, and is being subjected to widespread trials in the attempted control of bovine mastitis. Only 16 of 236 cultures of streptococci and staphylococci were able to grow in the presence of 0.125 Oxford units, and little evidence was found to suggest change in resistance to penicillin during or after penicillin therapy.<sup>19</sup> Several factors appear to influence the concentration of penicillin in milk,<sup>20</sup> and it does not seem, as reported earlier, that the concentration varies inversely with the volume of milk secreted.<sup>21,22</sup> Much current work is devoted to dosage levels, but the concentration in the mammary gland eight hours afterwards does not appear to justify some of the higher levels advocated.<sup>23</sup> Penicillin appears to be more efficient and less irritant as an udder infusion than sulphanilamide,<sup>24</sup> but a combination of penicillin and sulphamezathine has been advocated for this purpose.<sup>25</sup> There are, as yet, difficulties in the application of penicillin therapy to mastitis ("Summer mastitis") associated with *Corynebacterium pyogenes* infection, despite the fact that the causal organism is penicillin-sensitive.<sup>26</sup> Penicillin has been employed with success in the hitherto unyielding pyelonephritis of the bovine,<sup>27,28,29</sup> and although relapses usually occur it may well prove economic in salvaging a cow for one or more lactations.<sup>30</sup> Attention may be drawn to the value of penicillin in *Leptospira canicola* infection in dogs,<sup>31</sup> as well as in many types of bacterial infection in this species.<sup>32</sup> The inactivation of orally-administered penicillin in the dog may be reduced by the simultaneous administration of protective agents, amongst which protein agents (e.g., skimmed milk powder) were found to permit of absorption without untoward effects.<sup>33</sup> The penicillin treatment of early field cases of *Erysipelothrix rhusiopathiae* infection in turkeys would appear to be a practical possibility,<sup>34</sup> and further experimental work on this subject has been promising.<sup>35</sup>

### Streptomycin

Bovine strains of tubercle bacilli appear to exhibit the same order of sensitivity to streptomycin as do those of the human type.<sup>36</sup> Clinical trials of this antibiotic mainly await publication, but it has been claimed as effective, although on unconvincing evidence, in the treatment of calf pneumonia.<sup>37</sup> Although it proved effective when administered prior to, or simultaneously with, *Pasteurella multocida* inoculation in turkeys, if treatment were delayed for 6 to 24 hours, there were carriers and cases of joint involvement.<sup>38</sup>

### Mepacrine

Twelve cases of bovine coccidiosis were successfully treated with mepacrine hydrochloride [2-chloro-5-(5-diethylamino- $\alpha$ -methylbutyramino)-7-methoxyacridine dihydrochloride].<sup>39</sup> When used in a dosage of 1 g.

per 200 lb. body weight there were no toxic effects, and the low cost of treatment, as compared with sulphonamide compounds, was noted.

### Phenanthridium compounds

Field trials have been carried out in a number of African territories with two potent trypanocides, viz., phenanthridium "1553" (dimidium bromide) and phenanthridium "897" (a derivative of phenanthridium chloride).<sup>40,41,42,43,44,45</sup> Full evaluation of their rôle in protecting cattle in tsetse fly areas has yet to be made, but in one trial cattle initially in poor condition were introduced into and maintained successfully for 14 months on good grazing, in a medium tsetse area, when treated with "897." Reports from field workers upon the toxicity for bovines of phenanthridium compounds, in particular "1553," have been critically discussed.<sup>46</sup> It appears that variations did not occur in the toxicity of samples of "1553" supplied to field workers, and that toxic phenomena encountered in different parts of Africa and in different herds of cattle in varying states of nutrition must have been due to other causes. Pharmacological experiments upon laboratory animals and cattle<sup>46</sup> have indicated a striking similarity between "897" and "1553"; the only significant difference appeared to be in the concentration in the blood stream detectable in cattle, for while both persist for some 24 hours the concentration of "1553" is twice as great as that of "897." In laboratory experiments and in cattle<sup>47</sup> "1553" appears to be about three times as potent as "897" against *Trypanosoma congolense* infection. While "1553" appeared to be active against *T. congolense* and *T. vivax* in cattle, it was effective against only *T. vivax* in pigs, and was ineffective against *T. brucei* in either species.<sup>43</sup> Pigs affected with *T. simiae* appeared to withstand repeated dosage with "1553" and in them natural infection became of a chronic relapsing type.<sup>47</sup>

### "Antrycide"

It has very recently been announced<sup>48</sup> that 4-amino-6'-(2'-amino-6'-methylpyrimidyl-4'-amino) quinaidine-1:1'-dimetho salts, for convenience referred to as antrycide salts, possess marked trypanocidal activity. It has been stated that they may be administered subcutaneously with ease and safety and, in single doses, have cured infections of *Trypanosoma congolense*, *T. vivax*, and *T. brucei* in cattle, *T. brucei* in horses, donkeys, and dogs, and *T. evansi* in camels. They are stated further to have afforded considerable protection to cattle against subsequent infection with *T. congolense* and *T. vivax*. The publication of full details of these and later experiments will be awaited with great interest.

### "Nitrogen-mustard" compounds

Intravenous administration of 2 mg. of di-(2-chloroethyl)amine per kg. body weight was claimed to result in a small proportion of permanent or temporary cures in young chicks which had developed various syndromes consequent upon the administration of Beltsville strain, *A. leucosis*, virus.<sup>49</sup>

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# STARCH

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THE starch supply position in the United Kingdom continues to be difficult. Industrial requirements are on the increase and demands are in excess of available supplies. The question of available supplies of starch and its raw materials is bound up with that of hard and soft currencies, and unless the supply position improves Government control might have to continue for some time.

It is of interest to consider briefly the position of the various industrial starches. Supplies of farina, or potato starch, from soft currency areas are increasing. In the case of maize starch, home production is at its maximum and there are no imports from hard currency areas. Malaya is our main source of supply of sago flour and since that colony has been able to earn hard currency, the United Kingdom has not been in the market. The position is improving, however, and it is hoped that we shall be receiving offers in due course. The main supply of tapioca flour (Cassava) is from Indonesia. It is unlikely that appreciable supplies from this source will be available before the political troubles there are settled. As a result of colonial development, however, cassava starch of good quality, from Empire sources, is a possibility within the course of the next few years. As far as rice starch is concerned, as long as the world rice position remains precarious, supplies of this starch are not likely to increase. Home production of wheat starch is sufficient to meet present needs and there is no importation of this commodity.

The reviewer is indebted to the Director of Starch of the Ministry of Food for this picture of the starch position in relation to United Kingdom needs.

Since the last Report a large number of contributions to starch literature has appeared. Whilst the more fundamental aspects have been dealt with by contributors in various parts of the world, the industrial developments have mainly taken place in America and on the continent of Europe. The British Empire contributions have been noticeably small, a situation which should cause some concern. It is true that this country, apart from potatoes and wheat, does not grow the necessary raw materials, but in this respect it differs only in degree from Holland and other European countries. It is equally true that, in America, maize, wheat, and sweet potato sources provide a material stimulus to investigations on the production of starch and its derivatives. It is probable that a closer liaison in this country between industrial starch manufacturers and workers in independent research centres would be most beneficial, particularly in the direction of developing specialised starch products for the various industries which use starch. In this connection it is of interest to note a recent publication of the Food and Nutrition Board of the National Research Council of the U.S.A.<sup>1</sup> Among other things, this report sets out the nature of the work on starch being carried out

in a number of laboratories in U.S.A. and gives the location, and names of the personnel, of the laboratories in question.

### Manufacture

Investigations dealing with manufacturing problems largely refer to processes applied to corn and potato starches. Rice starch manufacture is still unfortunately restricted not only on account of the shortage of rice for this purpose, but also, as far as the United Kingdom is concerned, of the unreplaced factories destroyed during the war.

W. W. Howerton and R. H. Treadway<sup>2</sup> publish some revealing figures comparing the yield of potato starch in two factories, one of which employs a batch settling-process, the other using continuous starch settling-tables. In each process, steeping, grinding, screening, and drying operations are continuous. The completely continuous process produces the higher starch yield (85% as compared with 71%), the difference, as would be expected, being due to the method of purification. The waste liquid from the continuous process contains 24% starch and 32% protein, whilst in the batch-settling process, the liquor contains 45% starch and only 28% protein. P. M. Heertjes and E. E. Hekman<sup>3</sup> examine the question of the purification of this waste liquor from potato starch manufacture and express the view that if a cationic exchanger could be adapted to large-scale production successfully, the problem of purification of this liquor would be largely solved.

Yield and colour are always in the fore-front of considerations by starch manufacturers and consequently any procedures which favourably affect these factors are welcomed. G. Fukas<sup>4</sup> treats potato mash after the first extraction with NaOH to attain a  $p_H$  of 7.4–8 and by this means he claims to raise the total starch yield by 25%, at the same time achieving a whiter product. The same author<sup>5</sup> describes a way of using profitably the starch-protein by-product in the effluent by mixing it with extracted mash. He claims that this mixture is almost as good a feeding stuff as maize, and considerably cheaper.

I. S. Uppal<sup>6</sup> describes production in a maize starch factory and, in the process of emphasising the importance of chemical control, he provides production and chemical analysis data. H. K. Murer and W. A. Mitchell<sup>7</sup> have evolved a modified process for the extraction of starch from grains such as maize, wheat, sorghum, and rice. Whilst in standard starch processes the grain is soaked in a whole or kibbled state, these authors grind their grains into flour and mix with water to jellyfy the protein, and form a flowing slurry. This is passed through a colloid mill and the gluten gel is thus converted into a sol. The liberated starch granules are separated centrifugally, and dried. In order to inhibit bacterial growth the  $p_H$  is adjusted to 3–5, prior to drying, by the addition of an acid, preferably sulphurous acid; and the use of an anti-oxidant, such as gum guaiac, is suggested in order to prevent oxidation.

The first essential process in industrial starch manufacture consists in steeping with the object of disrupting the protein net-work of the grain. J. A. Waggoner<sup>8</sup> makes a study of this process in the case of maize starch. He examines the steeped grain by preparing cross-sections with a freezing microtome, clearing the starch with chloral hydrate, and

staining the protein and cellulose differentially with thionine. He shows that the lactic acid phase of steeping softens the corn by absorption of water. Later, a high concentration of sulphurous acid disrupts the protein matrix, leaving the protein massed against the cellulose cell walls. Additional steeping loosens the protein from the cell walls. This disruption of the protein net-work occurs more rapidly in freshly harvested grain than in grain stored for a year. Concerning the water absorption by maize grain, N. N. Hellman and E. H. Melvin<sup>9</sup> produce evidence that this is the same in spite of different origins of the maize, varying sulphur dioxide concentrations in the steeping liquor, and different storage times.

A. A. Thornton<sup>10</sup> describes his process for starch separation in which a drum centrifuge is used, and the fibres and starch slush removed by a scraper, which may be activated by a photo-electric cell. The scraper is automatically stopped when the white starch appears.

The recovery of gluten from wheat in an undenatured and unhydrolysed form is the subject of a patent by J. H. Obey.<sup>11</sup> He extracts wheaten flour with water containing sodium *o*-hydroxy benzoate and ammonia at 20° c. for 1 hour followed by the addition of acetic acid to the supernatant liquor to precipitate gluten.

In view of the explosive nature of starch dust, starch manufacturers will find data of considerable interest in the work of P. C. Bowes, J. H. Burgoyne, and D. J. Rasbash.<sup>12</sup> These authors have studied the inflammability in suspension of mixtures of combustible and incombustible dusts. They find that, in general, alkali salts are more effective flame suppressors than insoluble mineral salts. Alkali halides are specially effective, potassium being superior to sodium, and sodium bicarbonate better than limestone.

### Sources of starch

The results of the continual search for new raw materials suitable for starch manufacturers always command interest. The problem is not merely to find possible raw materials containing substantial amounts of starch. In order to achieve economic extraction, not only must the starch be suitable for industrial purposes, but also the by-products should desirably be such as to possess a useful market value. It is with these points in mind that one views the various suggestions put forward.

E. Lehman<sup>13</sup> evaluates horse-chestnuts, which contain 24–44% starch. This is a low proportion for a starch raw material, unless the by-products promise to be valuable. This starch may be separated from the crushed kernels by means of acidified water. When deprived of its bitterness, the starch is useful food and can be hydrolysed and fermented to give alcohol and a residue of cattle food. H. N. Barham<sup>14</sup> describes the removal of colour from sweet-potato starch, its adaptation to many commercial uses, such as manufacture of dextrins and adhesives, and its capacity to replace tapioca in nearly all its uses. G. Haskell<sup>15</sup> gives an account of maize genetics in the U.S.A.

Biological syntheses of starch-like substances are not to be overlooked, in spite of the fact that their commercial significance at the moment might appear to be slight. E. J. Hehre<sup>16</sup> has published a paper in which he describes the synthesis of amyloses and amylopectin-like substances by

means of bacteria or their enzymes. This type of synthesis is likely to assume a greater importance in view of the growing tendency industrially to distinguish between the properties of amylose and amylopectin respectively from common grains.

G. F. Sprague and M. T. Jenkins,<sup>17</sup> in a paper surveying the development of waxy-corn for industrial use, review studies on its physical and chemical properties.

Other investigations, in their early stages, concerning the extraction of starch from wild bananas, are reported from Kenya Colony.

### Special and modified starches

The treatment of starch to modify its physical and chemical properties is still engaging attention, although the past year has not been perhaps as fruitful in its results as have previous normal years. Nevertheless, this type of industrial research will continue to be of great importance as the various requirements of starch for specific operations become more defined.

D. W. Hansen<sup>18</sup> describes his process for producing a thin-boiling starch. He treats a maize starch suspension at 52° c. for 1 hour with an aqueous mineral acid solution and chromium trioxide, followed by the addition successively of sodium bicarbonate and acid. This gives a thin-boiling starch of controllable viscosity.

Starch with a lowered gelatinising and pasting temperature is produced by the Corn Products Refining Co. by heating a suspension of starch with water containing 15% of an alcohol.<sup>19</sup> The same Company<sup>20</sup> describes the preparation of dried soluble amylose. The amylose is obtained in a moist condition by fractional precipitation with butyl alcohol. In order to prevent it from becoming insoluble during drying, all the water is removed by successive treatments with an organic water-miscible liquid, such as methyl or ethyl alcohol, or acetone; after which the amylose may be dried spontaneously.

J. K. H. Seiberlich<sup>21</sup> claims a process for the preparation of starch films which are cheaper and more uniform than cellulose films. To achieve this he treats starch below the gelatinisation point at  $p_H$  7-8.5 with dilute sodium hypochlorite solution. The starch is washed free of hypochlorite, resuspended in water at 50° c. and gelatinised suddenly by adding excess of boiling water. The solution may be used as a size or dried into films on a drum dryer after the addition of a hygroscopic agent.

H. H. Schopmeyer<sup>22</sup> uses waxy-maize starch to produce tapioca-like substances resistant to disintegration on cooking. He pastes the waxy-maize starch at about 70° c. in the presence of 40% water, and follows this by shaping the paste into granules and drying.

R. W. Kerr and N. F. Schink<sup>23</sup> modify root starch by treating starch milk with sulphuric acid to  $p_H$  1.6-2.5 and then with formaldehyde or acetaldehyde. The temperature is maintained lower than gelatinising temperature for 3-28 hours, and the whole is brought to  $p_H$  6.3-7.0 by sodium hydroxide and sodium sulphite is added to react with the free aldehyde. Water is removed by filtration and the starch dried. This resultant starch is presumably of the non-swelling variety.

Chlorination of starch is studied by H. N. Barham and T. R. Thomson.<sup>24</sup> By oxidising the starch with excess of liquid chlorine they reduce the destructive effect of the hydrochloric acid produced. The reaction proceeds only reluctantly beyond the dichloride stage. The significance of this work is not only in its value in throwing further light on the nature and structure of starch, but also in the production of potentially useful reactive derivatives of starch. It may be of interest to record the fact that M. Kradjčinovič<sup>25</sup> has studied the oxidation of starch by using hydroxylamine to test for  $\text{-CO-}$  groups and diamines for  $\text{-CO}_2\text{H}$  groups.

Of general interest is a paper by J. P. Casey,<sup>26</sup> who discusses the use of starch in the paper industry, with particular reference to its future uses and developments of water-resistant, glutinous, and pre-gelatinised starches.

### Starch ethers and esters

M. Samec<sup>27</sup> has reviewed the formation and properties of starch esters and ethers; and has determined their molecular size, calculated chain lengths, and has provided a summary of his experimental methods.

The Dutch Co. of W. A. Scholten's Aardappelmeelfabrieken has been active in producing patents for processes for preparing ethers and esters of starch. In the first,<sup>28</sup> starch is dissolved in an anhydrous medium such as formic acid or a mixture of ammonium acetate and acetamide. The solution is treated at  $140^\circ\text{C}$ . with a mixture of an acid (such as lactic or acetic) and an acid anhydride (acetic anhydride) in the presence of an acetate. The water formed in the reaction is distilled away. The product ultimately isolated by the addition of water is soluble in organic solvents and contains more than 2.5 acyl groups per  $\text{C}_6\text{H}_{10}\text{O}_5$  molecule. A triacetate may be obtained by the addition of hydrogen peroxide. In the second process<sup>29</sup> starch is mixed with not more than twice its weight of water, an etherifying or esterifying agent (such as methyl sulphate or chlorosulphonic acid), sodium hydroxide, and optionally an organic solvent such as chloroform. The mixture is heated to remove water and to gelatinise starch. During heating the mixture is subjected to mechanical pressure on a rotary drum to give a thin layer which is immediately broken up. The resulting products are soluble in hot and cold water.

Allyl starch is prepared by J. Chadapaux, G. Champetier, and E. Savostianoff<sup>30</sup> by allowing potato starch to react with allyl bromide in methyl ethyl ketone in the presence of aqueous potassium hydroxide. The allyl starch thus produced is stable, but, like drying oils, in the presence of 0.2% cobalt naphthenate, it is auto-oxidised to a durable brittle resin.

### Analysis

The formulation of a reliable method for estimation of starch in grains and mixtures, capable of general use, would be most acceptable to analysts. Whilst no generally accepted method is yet available, individual workers are compelled from time to time to devise methods for particular purposes and such methods are seized upon for critical examination to widen their application. Thus, J. Terrier and J. Deshusses<sup>31</sup> review available methods for the estimation of starch in faeces, and describe

Terrier's method<sup>32</sup> in which faeces are extracted first by 80% and then by 95% alcohol to remove acidic substances. In the case of faeces, a correction is necessary for small amounts of non-starchy substances determined as starch. J. Grossfeld<sup>33</sup> describes his method for the estimation of soluble starch in flours intended for infants. This method is based on the precipitation of the starch by means of tannin, lead acetate, and potassium ferrocyanide. J. Kamecki<sup>34</sup> examines partially hydrolysed potato starch and has given its analysis and viscosity.

Of considerable interest is the work of K. A. Clendenning,<sup>35</sup> who is continuing his examination of the various factors involved in the determination of starch polarimetrically in cereal products. In the fifth paper on this subject, he examines the particle size and extraction time requirements. He finds that the precision, apparent starch content, and extraction time requirements are not influenced by finer grinding, but that the pentosan content of the calcium chloride extract is increased. Preliminary alkali treatment before calcium chloride extraction decreases pentosans. He gives polarimetric procedures for starch in whole wheat and wheat flour.

The microscopical examination of starch can be of much use to the analyst, particularly for the estimation of starch in pharmaceutical products and drugs. A study by means of the microscope of certain commercial and vegetable drug starches is made by R. L. Proper and H. W. Youngken.<sup>36</sup> In their method, a saturated solution of zinc sulphate is used as a suspending medium and eight counts of starch granules are made on a Ling blood-counting slide and averaged. Factors are derived for each type of starch from specially prepared suspensions of authentic samples.

The examination of amylase activity has such a close relationship to the reactions of starch that the work of P. Bernfeld and M. Fuld<sup>37</sup> is worthy of record. In two papers they describe a simple and rapid method for estimation of  $\alpha$ -amylase activity by comparing the iodine colour produced with amylase-degraded starch with a standard colour scale. They obtain a precision of  $\pm 5\%$ . They proceed to study the reducing power and change of iodine colour produced when  $\alpha$ -amylase from various sources (hog and human pancreas, human saliva, *b. subtilis*, and prepared malt  $\alpha$ -amylase) act on soluble starch and find it is the same for all sources. The application of this method, relating reducing time to concentration of starch, might result in a practical analytical procedure for starches in grains and mixtures.

### Chemical properties

In the last report it was evident that from an industrial point-of-view, the difference between the amylose and amylopectin fractions of starch was assuming increasing importance. This is further emphasised by the attention which has been paid to these fractions in the literature during the past year, and particularly to the task of effecting separation for industrial purposes.

Until a few years ago the method usually adopted for the separation of amylose from amylopectin was that of T. Schoch.<sup>38</sup> This involved a high temperature treatment, under pressure, of starch paste with butanol

and *isoamyl* alcohol. This method is known to cause some degradation of starch. In 1946 W. N. Haworth, S. Peat, and P. E. Sagrott<sup>39</sup> published a modified method. After boiling the starch in water and cooling, they precipitated the amylose with thymol and the amylopectin with methylated spirit. They pointed out at the time that cyclic alcohols, including *cyclohexanol*, are useful for the preparation of pure amylopectin. The continuation of this work appeared recently,<sup>40</sup> indicating the application of thymol and *cyclohexanol* for the preparation of pure amylose and amylopectin respectively. R. H. Hopkins and B. Jellinek<sup>41</sup> use a similar process to that of Haworth and co-workers. They separate amylose from amylopectin by the successive additions, on alternate days to non-autoclaved starch, of *cyclohexanol* and thymol. They further point out that the blue value of the amylose is greatly influenced by the method of recrystallisation from butanol-saturated water and by the period of heating during redissolving.

An important preliminary communication on the conversion of the straight chain amylose into branched chain amylopectin is made by S. Peat, E. J. Bourne, and S. A. Barker.<sup>42</sup> The conversion is carried out by means of an enzyme, not phosphorylase, from potato juice. This enzyme was first isolated by W. N. Haworth and his co-workers.<sup>43</sup> The authors' further reports on this significant work will be awaited eagerly as they may throw much light on a number of facts relating to amylose and amylopectin ratios in natural sources of starch, particularly during the period of growth. Thus, although as T. G. Halsall, E. L. Hirst, J. K. N. Jones, and F. W. Sansome<sup>44</sup> point out, there is no significant difference in the properties of amylose and amylopectin of two varieties of potato during growth, and that amylopectins from the two varieties are the same, nevertheless, any variation in the ratio of these two fractions during growth will undoubtedly greatly affect the properties of the extracted starch. Although little work as yet would appear to have been carried out on this variation, M. J. Wolf, M. M. MacMasters, J. E. Hubbard, and C. E. Rist<sup>45</sup> compare starch from maize at various stages of kernel maturity. These authors limit their examination to total starch content and find that the most rapid increase occurs from 12-20 days after pollination. The starch granule size increases from about 3-9  $\mu$  in the period 13 days after pollination to grain maturity. The water binding capacity of the starch decreases with maturity and immature starch has a low amylose content. The amylose contents of maize starches from North, Central, and South American sources have been estimated by R. L. Whistler and P. Weatherwax,<sup>46</sup> who find a variation of 22.2-28.3% on the fat-extracted endosperm.

Whilst discussing this question of amylose-amylopectin ratios, it is of interest to record an opinion expressed by R. Sutra<sup>47</sup> that starch is a homogeneous product. He considers that amylose and amylopectin are degradation products of starch and disputes the usefulness of methylation methods for the determination of chain length and branches. Root and seed starches are, according to Sutra, different types.

J. E. Hodge, E. M. Montgomery, and G. E. Hilbert<sup>48</sup> study the conversion of various starches to the limit dextrin stage with  $\beta$ -amylase. The starches employed are maize, wheat, sweet and white potato, and

tapioca. In each case the branch-chained amylopectin fractions are similar in the extent of their conversion. Whereas, however, root and tuber limit dextrins contain phosphorus, cereal limit dextrins do not. In the case of maize and sweet-potato starches, a fraction intermediate in extent between the straight-chained amylose and branched amylopectin is considered to be present to the extent of 5–8%. The existence of such a fraction may possibly provide a clue to unexplained minor variations in yields of starch sometimes experienced in industrial extractions.

T. M. Back, W. H. Stark, and C. C. Vernon<sup>49</sup> bring evidence to indicate that the amylopectin from maize starch (79% amylopectin) differs from that from waxy-maize in that it is more readily converted to fermentable sugars and gives higher yields than that from waxy-maize starch (100% amylopectin). The view that the amylopectins from various starches differ is supported by Samec.<sup>56</sup>

In an examination of the starch from the wrinkled and the smooth pea, S. Peat, E. J. Bourne, and M. J. Nicholls<sup>50</sup> find that the wrinkled pea starch contains 98% amylose and 2% amylopectin, and that from the smooth pea 30% amylose and 66% amylopectin.

The starch iodide reaction mechanism continues to be a subject for interesting study. N. C. Turner<sup>51</sup> uses radioactive iodine and his work leads him to the view that the change leading to the blue colour is induced in starches by iodine acting catalytically in the presence of oxygen and that the blue colour is not dependent on the presence of iodine. Against this is the work of A. K. Rai Choudhury,<sup>52</sup> which supports the view that iodine is chemically bound to starch. He bases this conclusion on a study of the effect of iodine solvents on the complex.

The photochemical degradation of starch is referred to in a preliminary communication of S. Peat, E. J. Bourne, and W. J. Whelan.<sup>53</sup> When they expose amylose in dilute solution to ultra-violet light of wavelength 3660 Å., with a trace of zinc oxide, the amylose is degraded to form formaldehyde, formic acid, and carbon dioxide. For wavelengths less than 3660 Å. zinc oxide is not necessary. It is an aerobic oxidation and in purified nitrogen, degradation is very slow, neither formic acid nor carbon dioxide being produced.

From France H. Brun<sup>54</sup> gives a review of the composition and chemical structure of starch.

### Physical properties

The physical properties of starch, including particularly measurements of viscosity and gel-strength, are of much industrial importance, and fully merit the attention given to them by numerous workers.

*Viscosity.*—M. Samec and M. Ferlan,<sup>55</sup> from Yugoslavia, examine the effects of salts of different cationic valency on the viscosity of amylose sols, and have shown that the decline with time of the viscosity depends upon the valency of the cation. Samec<sup>56</sup> also concludes that although amyloses prepared from different starches are identical, this is not so with amylopectin. In an examination of the isomerism of amylopectins, they describe differences between amylopectin prepared by electro-dialysis from potato and maize.

J. Jensen,<sup>57</sup> in his examination of the properties of starch-finishing pastes, considers the colloidal chemical properties of wheat and potato starches, including pasting, viscosity, swelling, and adhesive power with the object of finding optimum conditions for the finishing of textiles. He concludes that commercial wetting and emulsifying agents affect viscosity, and degree of swelling differently for different starches. A. Engblom,<sup>58</sup> also with usefulness in the textile industry in view, considers the viscosity of potato starch solutions and the behaviour of these solutions on enzymic and chemical degradation respectively. The viscosity is dependent on the ions present and is affected also by the purity of the water used. For finishing textiles with starch pastes Engblom considers that enzymic treatment is more effective and economical than chemical degradation.

E. K. Fischer and C. H. Lindsley<sup>59</sup> carry out rheological measurement on starch pastes, using a modified Stormer viscometer and present their data as graphs and tables.

W. G. Bechtel and C. C. Kesler<sup>60</sup> study the use of an automatic viscometer to study the starch pastes with special reference to the paper industry. The viscosity of starch varies with the rate of shear used in the test and with the previous treatment given to the sample. The automatic viscometer used by them enables the effect of cooking conditions,  $p_H$ , and cold-flowing properties of starch to be studied.

L. B. Crossland and H. H. FAVOR<sup>61</sup> follow the rate of swelling of a variety of starches (maize, wheat, potato, waxy-maize, tapioca, and wrinkled pea) in a dispersion medium of sodium alginate instead of water by means of viscosity measurements on an amylo-graph. They observe that maize and potato starches show marked difference in rate of swelling of granules in different temperature ranges.

The stiffening of potato starch is different from other commercial starches, according to A. H. A. de Willegen, J. Hofstee, and P. W. de Groot.<sup>62</sup> This is on account of the greater swelling capacity of potato starch granules which gives a higher peak of viscosity. These values can be lowered by conditions of manufacture and by storage in air.

H. J. Selling and F. L. J. Lamoen<sup>63</sup> describe a viscosi-graph for the continuous measurement of the viscosity of starch pastes. This involves the rotation of the freely suspended housing of a synchromotor rotating a stirrer at a given speed.

*Starch-gels.*—A review of the structure and swelling of starch grains is given by N. P. Badenhuizen.<sup>64</sup> R. T. Whittenberger and G. C. Nutting<sup>65</sup> examine the properties of potato starch-gels in relation to the effects of temperature, concentration,  $p_H$ , heat-moisture treatment, H-bonding agents (sucrose, dextrose, and glycerol), and electrolytes. Their results are shown in graphs, tables, and photomicrographs.

W. J. Hamer<sup>66</sup> has evolved a mercury balance method for the measurements of gel-strength. He determines the weight of mercury required to pull a standard brass disc from the gel in which it is embedded and provides details of his method. The same author<sup>67</sup> has studied the gel-strength of starch-flour gels in order to throw some light on the electrical behaviour of dry cells, particularly in respect of storage life. The reactions between the paste wall (starch-flour gel), the cell electrolyte, and the

manganese dioxide depolariser are studied by examining retarding effects of thirteen different types of starch, modified starch, and flour and starch fractions on these reactions. Only the flour fractions, gliadin and mesonin, produce an increase of electrical output.

The effect of electrolytes on the swelling of cereal starches forms the subject of a communication by R. H. Harris and O. Banasik.<sup>68</sup> They find that swelling of maize starch is increased by dilute caustic soda, hydrochloric and sulphurous acids, chlorine, aluminium sulphate, and thorium nitrate; and it is decreased by sodium chloride and magnesium sulphate.

O. C. Beckord and R. M. Sandstedt<sup>69</sup> describe a simplified equipment for the study of starch-gelatinisation by means of light transmission. A suspension of starch is circulated vigorously in a U-tube and heated at a known rate by a coil of resistance wire wrapped around the tube. Gelatinisation is followed by the measurement of light transmission through the starch suspension.

For the simple determination of cold water adsorption capacity of pregelatinised flour, L. Klee, L. Sair, and L. A. Hall<sup>70</sup> base their technique on volume of the centrifuged flour-water pastes and they use this technique for the evaluation of cold water adsorption capacity of unprocessed and gelatinised wheat and maize flours.

In an examination of maize amylose, K. H. Meyer, P. Bernfeld, P. Gürtler, and G. Noelting<sup>71</sup> find that it contains fractions of high molecular weight (340,000) as well as low (10,000–50,000). The high molecular weight fraction is absent from potato starch, and this accounts for the fact that maize starch size solidifies more rapidly than potato starch size.

L. H. Lampitt, C. F. H. Fuller, and N. Goldenberg<sup>72,73</sup> continue their fundamental investigation, mainly physico-chemical in nature, on the fractions from potato starch. They have examined the molecular weights, viscosities of hot and cold water fractions of de-polymerised potato starch caused by grinding, and compared the values with those previously obtained from wheat starch. The viscosities of the potato starch fractions are higher than those of the corresponding wheat starch fractions, that of the hot-water potato starch fraction being particularly high. The viscosities are approximately proportional to the mean molecular weight of the fractions. With G. H. Green<sup>74</sup> these authors have examined the retrograding properties of these cold and hot water fractions of potato starch. They are quantitatively not unlike those of wheat starch fractions. The difference in the retrograding properties of these starches seems to be governed by their contents of amylose and amylopectin, and by the nature and distribution of the phosphorus. Most of the phosphorus of the potato starch fractions is bound to the starch,<sup>75</sup> and is not split off during precipitation of starch by alcohol. Potato starch amylopectin contains much more phosphorus as ester-free phosphate groups than the corresponding amylose. In the case of wheat starch the reverse is the case, the phosphatides being preferentially absorbed by amylose.

An interesting review of factors affecting the strength of paper is given by S. R. H. Edge,<sup>76</sup> who provides data showing the effects of rice, maize, and potato starches on various physical aspects of paper.

### Saccharification

The continuous hydrolysis of maize starch is considered by J. E. Dlouhy and A. Kott,<sup>77</sup> who deal with some problems associated with the design and operation of the process.

F. J. Cleveland<sup>78</sup> uses sulphuric acid in place of hydrochloric acid for the hydrolysis and neutralises the acid with calcium hydroxide to prevent formation of sodium chloride. In their preparation of maltose syrups from wheat flour, A. Efron and R. H. Blom<sup>79</sup> first remove soluble protein by treatment with water, and then heat and strain the residue to render the starch more accessible to enzyme action. The resultant syrup is clarified with active carbon and bentonite.

H. H. Schopmeyer, F. J. Hammerstein and W. Larmouth<sup>80</sup> describe their heating process to produce a syrup free from developed flavour and colour, and containing 1-4% water.

In the production of conversion syrups H. Wegner<sup>81</sup> shows that ammonia and primary and tertiary amines are produced to the extent of 0.07-0.22% and he considers that spoilage odours in these syrups may be due to their nitrogen bases.

J. Corman and A. F. Langlykke<sup>82</sup> have studied the alcohol yields from fermentation of maize starch mash and in their view they correlate more closely with the potency of a glucogenic enzyme system rather than with fungal  $\alpha$ -amylase. The  $\alpha$ -amylase liquefies starch and converts it to dextrins and maltose, but the gluconic enzyme takes it to glucose. In spite of a low Lintner value of the mould cultures, the yield of fermentable sugars is as high as, or higher than, that obtained with a distillers malt sample.

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# SUGARS

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ONE of the most striking observations noted during the past year is the growing attention paid to by-products of the sugar industry and some of the developments will be referred to in the following pages.

According to Willett and Gray's<sup>1</sup> estimates world production for 1947-48 was slightly higher than that for 1941-42 and is likely to be substantially higher in 1948-49. The figures (in long tons) are as follows :

	1948-1949	1947-1948	1941-1942
Beet sugar ..	10,320,000 ..	8,782,739 ..	9,148,770
Cane sugar ..	20,898,800 ..	20,198,511 ..	19,262,747
	<hr/> 31,218,800	<hr/> 28,981,250	<hr/> 28,411,517

The expected increase for 1948-49 is looked for in the beet production in the Eurasian area.<sup>2</sup> It is likely that the Cuban crop will show a drop of 600,000 tons, so that there is a gradual change of the supply picture leading perhaps to an easing of the sugar restrictions in the soft-currency areas. It is thought by some that there may come a time after stocks have been built up when the industry will be over-producing. Thus the work at the present time on outlets for sugar other than for food, would appear to be well worth while.

## Cane sugar manufacture

### *Plant*

The healthy state of the engineering side of the industry can perhaps be best appreciated by a study of the advertisement pages of the trade journals devoted to sugar technology. It would appear that milling machines, juice heaters and evaporators, vacuum equipment, crystallisers, filters, centrifugals, etc., are the equal of those used in any other branch of the chemical engineering industry. Experience on a turbine mill drive in a Louisiana factory has been described by F. A. Vought and C. L. Savoie,<sup>3</sup> and useful notes on evaporator and vacuum-pan tubes have been provided,<sup>4</sup> cupro-nickel being the most resistant metal for use. Work in South Africa with the Oliver-Campbell mud filter has been outlined by R. D'Avic.<sup>5</sup> Throughout the world, 500 of these machines now appear to be in use, and although they are somewhat expensive, the advantages they offer are : continuous process with consequent large saving in labour, low sucrose content of the filter cake and the elimination of all operations with filter cloth. Notes on sugar factory boilers in Barbadoes<sup>6</sup> are valuable.

Comments have been made by Doss and Agarwal<sup>7</sup> on the reasons for the uneven distribution of sugar in cane and they suggest the isotonic polarisation as a new basis for milling control. Queensland experience

on cane preparation where crushers are not used is described by C. W. Waddell.<sup>8</sup> New features in a 15-roller milling plant for Peru are pointed out,<sup>9</sup> and the centrifugal washing of sugar is the subject of a patent.<sup>10</sup> Comments<sup>11</sup> have been made on the drying of raw sugar.

An informative article has been written by J. G. Davies<sup>12</sup> on the machinery and equipment in factories and distilleries in Jamaica and mechanisation in the sugar cane fields is the subject of a report from South Africa.<sup>13</sup>

### *Scale*

A good deal of attention has been paid to the question of scale in evaporators, its ready removal being a matter of some considerable economic importance. The phenomenon evidently presents some lively problems in colloid chemistry.

It is apparent that one approach is by actual prevention of scale deposition. This has been attempted by electrical methods which have been described by Willey,<sup>14</sup> and more recently by Springer.<sup>15</sup> The latter considers that the use of tetraphosphoglucosate (mentioned later) was a failure in Trinidad and claims that electrolysis methods, using preferably aluminium electrodes which alter the charge on the negatively charged cane juice colloids, can be made fairly successful. It is suggested that electronic devices could provide a solution of the scale problem. The electrical coagulation of cane juice has been studied by D. N. Ghosh<sup>16</sup> by a new technique consisting of two operations. Cold raw juice from the crushing mill is subjected to direct current using wrought-iron electrodes. When the  $p_H$  reaches 7.2, the liquid is filtered, then adjusted to  $p_H$  6.9 with superphosphate and evaporated. Curves depict the comparative study of electrical, double sulphitation, and carbonatation processes and the method is claimed to be economically sound. A case where the scale problem has actually been solved by choosing special operating conditions is described by R. L. Getty.<sup>17</sup> The composition<sup>18</sup> of cane juice has been studied especially in regard to  $p_H$  changes (4-6) with age and to the content and nature of acid components, aconitic, oxalic, malic, citric, glycollic, and tannic acids being assayed.

Analyses<sup>19</sup> of scale in the Frome factory, Jamaica, have been made and estimated as  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{P}_2\text{O}_5$ , and the method of cleaning involves the use of sodium hydroxide, sodium carbonate, trisodium phosphate, and hydrochloric acid. The cost of cleaning the 20,000 sq. ft. Frome evaporator was £65 per week per 15,000 tons of cane. It appeared (J. G. Davies<sup>12</sup>) that the amount of scale depended upon the amount of residual calcium which would be minimised by adequate phosphate content of the juice. In British Guiana ammonium fluoride was the only effective scale remover though use of trisodium phosphate was promising.

Analysis<sup>20</sup> of a particularly heavy scale which resisted open boiling with 5%  $\text{NaOH}$  for six hours and 1%  $\text{HCl}$  for three hours showed that it was a typical sulphate scale. The sulphate content of the clarified juice was 0.2 g. per 100 ml. and it was considered that the heavy scale was due to an excess of sulphates in the raw juice. The scaling might be overcome by increasing the  $\text{P}_2\text{O}_5$  content of the raw juice and by avoiding certain cane strains.

Numerous methods for the removal of scale have been described, some of them using proprietary scale removers. A convenient method is claimed by A. R. Yatheraja.<sup>21</sup> The scale is softened by boiling with a mixture containing 0.3% NaF, 0.3% HCl, 0.15%  $\text{NH}_4\text{F}$ . Scraping with an electrical outfit was necessary, but was easily carried out and gave cleaner surfaces.

The acid cleaning of boilers has been outlined,<sup>22</sup> while a novel idea<sup>23</sup> for increasing the efficiency of acids has been tried out. This makes use of the finding that complex aromatic amines added to acids give what are termed chemical "inhibitors," and they intensify the solvent action of acid on scale while lessening the action on metals. One pound of amine is used per 100 lb. of acid and it is claimed that the method is effective and is coming into use. The reagent known as tetraphosphoglucosate (T.P.G.) used as a scale preventive has generally received commendation. It is a green or yellow-brown viscous colloid having specific gravity 1.384 and, being soluble in hot water, with  $p_H$  5.9 (*e.g.*, see particularly C. W. Fitzwilliam and R. D. E. Yearwood,<sup>24</sup> who give a somewhat unlikely formula for the substance), the material forms suspensoids with metallic compounds in solution preventing them from precipitating and adhering as scale. Numerous advantages are credited to the use of this substance. L. N. Armstrong<sup>25</sup> gives an account of a discussion where various workers also find that T.P.G. is good and there is described the advantageous use of another preparation, "Sumaloid." Hawaiian experience with T.P.G. has been discussed.<sup>26</sup> It was the consensus of opinion that it provides at least a partial solution of a troublesome problem and it may open the way to long tube high velocity evaporators in raw sugar factories. C. W. Stewart<sup>27</sup> describes the successful use of T.P.G. in various American factories and also mentions another compound "Tetrafosforg" which was helpful and which will continue to be used. Yet another compound, "Wrikorg-C," has been investigated.<sup>28</sup> An investigation of the use of polyphosphates in scale prevention showed that they were of no value and that use of a colloidal treatment free of phosphate might prevent scale deposition. The "Wrikorg-C," consisting of a non-toxic mildly alkaline solution of a highly surface active organic colloid mixture was used at the rate of  $1\frac{1}{2}$  lb. per 100 tons of cane and was highly successful.

### *Bonechar*

A brief review<sup>29</sup> has been presented of the bonechar process in cane sugar refining and some of the fundamental problems in the filtration and revivication processes are outlined. It is suggested that the "rugged" characteristics of bonechar as an adsorbent have been responsible for its continued use for more than 50 years. The importance of bonechar was emphasised by the attention paid to it in a special investigation<sup>30</sup> carried out at the Bureau of Standards, Washington, where an attempt was made to gain an understanding of the fundamental structure of bonechar. Methods used were X-ray diffraction, electro-micrographs, density determinations, surface area measurements, chemical analysis, specific heats, and heats of wetting and combustion. The primary structure of the char was of a complex hydroxy apatite type, on which was

superimposed a secondary macro-structure derived from the original cellular composition of bone, the whole crystal lattice giving a very porous structure. It was possible to get an explanation in terms of altered crystal structure of the effect of excessive heat in decreasing the absorption power of the bonechar. A relationship between bulk density and absorptive properties may form the basis of a test for the value of a bonechar, especially after continued use. In view of these findings it is of interest to note<sup>31</sup> that a synthetic hydroxy apatite giving an X-ray pattern indistinguishable from that of bonechar, has been developed as a possible substitute for bonechar. Treatment of liquors with solid adsorbents such as bonechar is the subject of a patent.<sup>32</sup>

### Beet sugar manufacture

According to Czarnikow's sugar review for 1948 the United Kingdom sugar beet crop for 1947-48 amounted to 427,000 tons. An interesting report by a special mission on the mechanisation of the sugar beet industry in North America has been provided.<sup>33</sup> Attention is called to patents taken out on beet harvesters<sup>34</sup> and to other machines,<sup>35</sup> including a topping machine for root crops.<sup>37</sup>

Progress in beet sugar technology has been reviewed by R. H. Cottrell,<sup>35</sup> who reaches the interesting conclusion that ion exchange methods will replace all standard methods and will stimulate a whole new field of by-product recovery.

The present state of the important question of the beet seed processing programme in the U.S. has been reviewed by R. Banier.<sup>38</sup> Two new processes have recently been developed, namely burr reduction and decortication. It appeared desirable to use a combination of the two processes and processed seed appeared to be superior to segmented seed in almost every respect. Several commercial machines employing both new methods have been installed though special planting machines have to be used. J. Jackson has written an extensive paper<sup>39</sup> on a quantitative theory of the second carbonatation of beet juice. In this the lime salts figure at the optimum end-point calculated from the  $p_H$ , buffer capacity, ionic juice strength and known thermodynamic constants and suitable experimental results are quoted in support of the theory. The physical chemistry of the second carbonatation was also studied with artificial juices.<sup>40</sup>

### *Ion-exchange methods*

The BIOS report<sup>41</sup> on the purification of sugar juices in Germany showed that no remarkable progress had been made. Numerous experiences indicate the growing interest in ion-exchange resins, especially in beet sugar processes. Indeed, one article states that the ion-exchange process has matured.<sup>42</sup> Some remarkable advantages are claimed for the method, including the cutting out of activated carbon for white sugar production. There can be obtained a sucrose recovery of 95-96% and ash removal of 95-98% with consequent increased efficiency at evaporation stages. Numerous patents have been taken out on ion-exchangers.<sup>43</sup> Sorgo juice yields an edible final molasses obtained by the aid of ion-exchange.<sup>44</sup>

Experiences with two pilot-plant scale de-mineralisers have been described. The first<sup>45</sup> was used for cane-syrup and molasses, while the second<sup>46</sup> was used for Louisiana and Cuban cane-juices. In the latter paper the writer comments on the recent intense publicity given to ion-exchange methods which is some form have been known in the sugar industry for 50 years. In general, useful results were obtained but the water dilution requirements presented some problems though these were minimised by the fact that no scale-forming salts remained, so that continuous operations could be performed throughout the crop.

Valuable experience was obtained on the capacity of the resin beds. Italian experience<sup>47</sup> in sugar-juice purification by ion-exchange revealed that 15.5 g. of resin were necessary to remove 1 g. of non-sugar substances. With amberlite resins<sup>48</sup> on molasses considerable purification and lowering of ash content was achieved. First campaign results<sup>49</sup> of de-ionisation on factory scale in the Layton factory show an extraction of 92% for the time the de-ionisation equipment was in operation: it is expected to increase this to 96% during the next campaign.

### *Chromatography of sugars*

Many of the principles of adsorption, using, for example, forms of charcoal, bonechar, etc., have long been applied in the sugar refining industry. Now we are seeing the beginnings of the application of a special type of absorption, namely chromatography, which has probably been delayed until now by reason of the colourless nature of sugars. Binkley and Wolfrom<sup>50</sup> reported on a chromatographic method of isolating sucrose from molasses and now these authors have provided an excellent summary<sup>51</sup> of knowledge to date on applications of this valuable technique in the sugar group. General procedures in using this new tool, *e.g.*, the types of apparatus, choice of adsorbent, operation of the chromatogram, extrusion of the column, elution of adsorbed material, etc., are adequately described and details are given of different techniques as applied by various investigators to sugar mixtures. A few of these are worthy of special mention. Reich<sup>52</sup> chose coloured derivatives of glucose and fructose, namely the phenylazobenzoyl esters, adsorbed these on silica and eluted initially the less firmly held glucose derivative with a benzene-ligroin mixture. Tiselius<sup>53</sup> used the principle of the "flowing chromatogram," using a carbon column, and he studied the adsorption properties of a wide range of monosaccharides and later, with L. Hohn,<sup>54</sup> analysed mixtures of mono-, di-, and tri-saccharides. Jones,<sup>55</sup> in an elegant method adsorbed mixtures of methylated sugars on alumina and eluted the separate components with ether-ligroin mixtures. Wolfrom and colleagues<sup>56</sup> applied the brush technique of Zechmeister,<sup>57</sup> using permanganate and thereby provided a powerful weapon for detecting the sugar zones on a column. Other applications applied by Wolfrom and his colleagues are described in the monograph. Bell<sup>58</sup> separated various sugar ethers by a combination of extraction with partition solvents and flowing chromatography on silica-water columns while Gilbert, Smith, and Stacey<sup>59</sup> added an extra refinement to this method using jacketed columns for solvent extraction at elevated temperatures with chloroform-ligroin mixtures.

Chromatography of sugars can now be achieved on a micro-scale by use of the paper-strip method,<sup>60,61</sup> developed for amino acids. Adsorption on to starch columns is another valuable quantitative method now being explored by Dr. J. N. K. Jones.<sup>62</sup> Undoubtedly these methods will be valuable in the future in dealing particularly with sugar by-products, and it seems feasible to employ them on the large-scale. The methods have opened up new prospects in carbohydrate chemistry and will solve many problems in the complex structure of gums, mucilages and pectic substances.

### Molasses

Molasses continue to prove a valuable, and at the moment a rather high priced (three times pre-war) commodity, providing as it does the raw material for the fermentation industries.

The production of an edible treacle from molasses was the subject of a patent<sup>63</sup> in which it was claimed that lactic acid treatment followed by adsorption with wood or animal charcoal removed objectionable contaminants. It has been recommended<sup>64</sup> that the use of molasses as a fuel in Queensland should be discontinued in favour of its use as a fertiliser. An interesting article<sup>65</sup> was provided on the genesis of molasses. It is claimed that the decisive factors are saline substances, and decomposition products of sucrose and glucose. By making reducing sugar balances at each stage it is possible to maintain a control that will keep molasses at a minimum. The identification and isolation of the constituents of cane-molasses was undertaken by J. H. Payne,<sup>66</sup> who studied, in particular, the distribution of nitrogen in molasses and the isolation of nitrogen-containing components such as aspartic acid, glutamic acid, lysine, purine bases, etc. The voluminous data was carefully tabulated. An interesting article<sup>67</sup> has been written on the fermentation of molasses in the Arroyo process,<sup>68</sup> while a valuable contribution to rum-technology is the account<sup>69</sup> of R. Arroyo on straight light-rums from Blackstrap molasses. Precautions in the fermentation and distillation procedures are discussed. A research of high potential importance is the work of F. W. Zerban and C. Erb, who outline a method<sup>70</sup> for the production of fermentable sugars from unfermentable reducing substances in molasses. Acid treatment is used to hydrolyse the anhydro sugars and sugar amino acid condensation products to fermentable products. It is considered that large-scale experience is needed to determine the economy of the process. Australian production of alcohol from molasses is described by I. R. Sherwood.<sup>71</sup>

The use of molasses in grass silage preparation forms the subject of a most valuable monograph by C. B. Bender,<sup>72</sup> who provides an excellent bibliography on all aspects. It appears that the use of molasses as a preservative for green crops is a sound proposition for the dairy farmer in humid areas, for all pasture crops and green hay can be satisfactorily ensiled. The destructive action on weeds, comparative yields and the nutritive value of the silage is critically surveyed and the opinion expressed that with new equipment for harvesting, hauling, and so on, present-day costs will be substantially lowered with a consequent lowering of the cost of milk production.

### *Crystallisation*

A neutral suspension of lignin, preferably in alkali, provides<sup>73</sup> a useful reagent for clarifying sugar juice before crystallisation. According to H. E. Powers,<sup>74</sup> an item of an analysis previously neglected, namely the determination of the grist of sugars, is to be discussed at the 1949 International Commission for Uniform Methods of Sugar Analysis. In his interesting article recommendations, such as correct sampling, choice of sieves, operation of mechanical shakers, etc., are made to deal adequately with the grist of sugars. A useful 2-sieve (Tyler) table is provided. An elaborate apparatus for the continuous crystallisation of sugar is the subject of a patent.<sup>75</sup>

A fundamental study on the decolourisation of sugar juices by activated carbon and sulphur dioxide has been made by B. Freed and D. Hibbert.<sup>76</sup> These agents act independently at high temperatures and the amount of colour removed is a linear function of the amount of carbon added at all  $p_H$ 's. An extensive careful survey<sup>77</sup> has been made of the effect of factory conditions on crystal formation and methods have been worked out for correct sucrose deposition.

Observations<sup>78</sup> on the handling of low grade massecuites with numerous crystallisation hints will be found valuable. New fundamental work<sup>79</sup> is provided by a study by Miss Taylor of the solubility of pure sucrose in water and by a study<sup>80</sup> which correlates the viscosity, temperature, and concentration of sugar solutions. A useful patent on the purification of syrup is due to P. J. Gaylor,<sup>81</sup> using a method of solvent extraction in which the aqueous syrup solution is extracted by a water insoluble cyclic ether.

The effect of juice impurities on available sucrose was discussed by H. B. Springer, who showed<sup>82</sup> that the presence of salts affected crystallisation and regards it as necessary to examine soil salinity and correlate it with the analysis of the first expressed juice. Hypochlorite preparations seem to be coming into use for the decolourisation of sugar.<sup>83</sup>

### *Bagasse*

The excellent bibliography<sup>84</sup> on sugar cane bagasse was mentioned in last year's Report and it would appear that rather than use bagasse solely for fuel many of the proposed outlets and new ones are gradually being developed. Lathrop<sup>85</sup> states that about 20 million tons of bagasse are produced annually during the manufacture of cane sugar. The most successful application of bagasse is in the manufacture of insulating and hard board products of which about 2 million sq. ft. per day are being produced in U.S.A. alone. Owing to the springy character of its fibre, bagasse has an advantage over wood for making insulating boarding. Other uses in Louisiana are for plastics for gramophone records, for mulch and litter, and for paper-making. For the latter industry, only two small factories appear to be in operation since a number of technical draw-backs have yet to be overcome. Machinery for paper-making and boarding is advocated by one firm,<sup>86</sup> and there is undoubtedly a growing opportunity for bagasse utilisation. The composition of bagasse and its ash has been given by Almeida.<sup>87</sup> A novel idea<sup>88</sup> is the production

of oxidation products such as saccharic acids, dilactones, diamines, etc., from the glucose of bagasse.

### *Trash*

Trash consists of various types of leafy materials and immature joints of the cane which are normally removed by hand during harvesting. In a striking article on this topic, W. S. Daubert<sup>89</sup> states that the losses caused to the sugar industry by trash are so tremendous that the best brains are needed to develop methods of getting cleaner cane. With the prices of both sugar and molasses likely to decline the economic aspects of the trash-problem are serious. The same view is taken by C. W. Stewart,<sup>90</sup> who states that there is nothing to excuse the milling of trash with cane. The trash-problem was viewed from the chemical standpoint,<sup>91</sup> and analyses were made of the components of dead leaves, green joints, top leaf roll, etc., and it was concluded that trash constituents decrease the recoverable sugar by increasing the sucrose loss in bagasse and by introducing non-sugars which are supposed to be molasses-forming constituents.

### *Sugar cane-wax*

Balch's excellent monograph<sup>92</sup> summarises the present situation. This wax is a somewhat neglected by-product of the industry, which must engage the attention of chemists and industrialists in future years. It is estimated that the cane sugar factories of the continental United States, Hawaii, Puerto Rico, and Cuba throw away about 60 million pounds of cane-wax annually representing about 38 million pounds of useable dark hard wax and 22 million pounds of undeveloped fatty material. Solvent extraction and separation methods appear to be the best way of getting a uniform hard wax which can then be fractionated by direct crystallisation, ethanol or isopropanol being good solvents. The fatty fraction is a source of significant amounts of crystalline alcohols (sitosterols and stigmasterols), and fatty acids (60%). Cost figures appear to be reasonable. A patent<sup>93</sup> on the extraction of sugar cane-wax utilised the extraction of the dry pulverised press cake with four or more parts of a solvent just below its boiling point. The wax is separated from the chilled solution at 15°. A wide variety of mixed ketones and, mixed acetates were used, those with boiling point below 120°, *e.g.* isopropyl acetate, being preferred. One hundred parts of press cake (containing 70 parts each of wax and fatty material) gave 61 parts of wax.

### *Cane sugar cultivation*

Journals, particularly the International Sugar Journal, devoted to sugar technology, carry many fascinating reports on the sugar cane in various parts of the world. Many of these are worth noting for they consider such important aspects as weed control, cane diseases, insect pests, genetics, cane selection, and so on. The "Sugar Cane in Mauritius,"<sup>94</sup> for example, gives an account of the seedling, position, fertiliser trials, and of imported West Indian varieties undergoing trial. The "Sugar Cane in Barbados"<sup>95</sup> considers various aspects of cane cultivation, manurial trials, and of yields checked with rainfall statistics.

The "Sugar Cane in West Indies"<sup>96</sup> considers soil problems, cultivation systems, insect pests, etc., while other reports for India,<sup>97</sup> the Phillipines,<sup>98</sup> Peru,<sup>99</sup> Cuba,<sup>100</sup> give a good cross-section and indicate the alertness and research appreciation of those individuals directing the industry. The performance of new kinds of sugar cane has been discussed,<sup>101</sup> as well as the propagation of recently released varieties,<sup>102</sup> and also the flowering of various species.<sup>103</sup> Precise instructions for the successful germination of the sugar cane are given by C. Van Dillewijn.<sup>104</sup> Crop production and environment is ably discussed in a book by R. O. White.<sup>105</sup> A wealth of data on the effect of nitrogen on the sugar cane has been provided.<sup>106</sup> In general, increased nitrogen up to a point, gave increased total sugar, and many interesting correlations were made.

#### *Problems of insect pests, diseases, and weed control*

In many of the foregoing reports the above problems are prominent. A booklet<sup>107</sup> on insect pests of the sugar cane in British Guiana gives an account of the history, damage, control measures, and parasites of the principle sugar cane pests. Cane grubs can be controlled by gammexane. The moth borer continues to need firm measures<sup>108</sup> to keep it under control. Its natural parasitic enemy *Lixophaga diatracae* (in Cuba) and this and the *Amazon fly* (in Venezuela) hold out the best hope of a suitable remedy.

Great damage (15% of sugar produced) is caused by insect pests in Venezuela and these are difficult to control by insecticides. The Fiji disease has been critically surveyed by J. P. Martin,<sup>109</sup> who suggests suitable remedies and describes the work of a control station in Samoa. The disease is transmitted by the sugar cane leaf hopper and is characterised by dwarfing galls. Control of the leaf hopper, use of tolerant strains, preventive quarantine are remedies. Ring spot, mildew, chlorotic streak are less vital diseases but may occur in low-lying areas. Some of these in Mauritius and Queensland have been described,<sup>111</sup> and remedies suggested. "Carbon" disease and sugar cane varieties have been investigated.<sup>110</sup> Prevention of these diseases seems the soundest policy. The most recent practice in sugar cane culture, including weed control, is given by G. Arcencaux,<sup>112</sup> who advocates for the latter both spraying and flame throwers. In Mauritius H. Evans<sup>113</sup> finds that good results can be obtained by the dual action of hormones and herbicides which eventually must have a profound influence on weed control. Alligator weed on sugar cane can be controlled by 2:4-dichlorophenoxy acetic acid.<sup>114</sup>

#### **Special fermentations**

##### *Food yeast*

H. J. Bunker and colleagues<sup>115</sup> have described a method for maximum yeast production avoiding foaming and discuss the value of food yeast in nutrition. The development of the Teddington process for food yeast production at the Frome factory in Jamaica is the subject of a detailed article.<sup>116</sup> Production is satisfactory and the final product is a light cream-coloured powder with a pleasant meaty flavour. It contains 45-50% of protein, 2% phosphorus, the whole range of the B group of

vitamins and also beneficial minerals such as iron, magnesium, potassium and calcium.

In all respects the product conforms to food regulation standards and appears valuable. A complete specification of the Frome plant is provided. Experience of food yeast production in Natal<sup>117</sup> using the same process is given by F. O. Read.

#### *Dextran*

Gums in the sugar factory were the subject of a paper by M. Sainclivier.<sup>118</sup> Dextran was regarded in 1947 as being of sufficient importance for De Whalley and Scarr<sup>119</sup> to recommend the fermentation to dextran of waste waters from sugar beets. Dextran production by new strains of *Leuconostoc* have been described from two laboratories.<sup>120,121</sup> The use of dextran as a stabiliser for sugar syrups is the subject of an American patent,<sup>122</sup> while the need for dextran derivatives for this purpose and for a blood plasma substitute<sup>123,124</sup> has stimulated the large-scale production of dextran by deep culture methods.<sup>125</sup> Some possibilities of the applications of dextran were suggested by W. L. Owen.<sup>126</sup>

The causative agent of the viscous putrefaction of beets was shown to be a fructosan-former and was named *Phytomonas betae-gelatae*.<sup>127</sup>

#### *Micro-organisms in raw sugar*

De Whalley and Scarr<sup>128</sup> discussed this aspect in 1947. They considered that the origin of the contamination was the soil attached to the cane or beets. Losses of sugar were caused by acids or invertase produced by the micro-organisms such as *B. subtilis*, *B. mesentericus vulgatus*, *B. aerogenes*, and a number of others. Valuable methods for the control of these organisms were suggested. One of the disadvantages of large-scale ion-exchange methods may be due to sugar losses by bacterial infection<sup>45</sup> of the diluted solutions on the cation bed. On the other hand, recent experience<sup>129</sup> indicates that the resin beds actually act as filters removing some bacteria and destroying others and further regeneration rids the beds of accumulated bacteria. A recent report<sup>130</sup> on sucrose losses during manufacture discusses the activities of thermophilic organisms and advises cleanliness in refineries. The significance of the desirability of a low bacterial content in sugar mills has been further emphasised.<sup>131,132</sup>

In the corrosion of sugar beet diffusion batteries the microbiological aspects are discussed by L. A. Allen and A. Cairns.<sup>133</sup>

#### *Unfermentable reducing substances*<sup>70</sup>

This problem is ably discussed by L. Sattler,<sup>134</sup> who failed to find the two keto-hexoses which Lobry de Bruyn and van Ekenstein believed to be present in the unfermentable material obtained by treating glucose or fructose with alkali.

The term "glucose" applied to the unfermentable reducing substances from simple sugars or cane molasses is misleading. The products isolated include anhydro sugars and minor amounts of simple organic compounds formed by heat or fermentation. All these compounds can react with amino acids to form reducing complexes. Earlier methods of analysis are considered to be unsound. The latest work on this problem is by

F. W. Zerban.<sup>135</sup> The two previous authors in collaboration also discuss<sup>136</sup> glucic acid and the breakdown of sugar with special reference to spontaneous decomposition of molasses.

### Miscellaneous products

#### *Pectin*

Pectin production from beet is likely to become an industry of some importance. Methods have already been described<sup>137</sup> for extracting pectin and the purification process gives a product which readily meets commercial specification.

#### *Aconitic acid*

This also is likely to become a more valuable by-product since it could well be used in the plastics industry. A method for the determination of aconitic acid has been given,<sup>138</sup> and a process for calcium aconitate production adapted for commercial production.<sup>139</sup> A process has also been given for a laboratory preparation from evaporator scale.<sup>140</sup>

### The work of the Sugar Research Foundation

Under the able directorship of Dr. R. Hockett, the Foundation continues to make sound progress, the most recent account of which is given in the 1948 publication "Science Looks at Sugar."<sup>141</sup> Up-to-date news of the Foundation's activities is provided by its quarterly publication, "The Sugar Molecule." The July 1948 issue announces that over a million dollars has already been allocated in research grants.

The sixty or more projects in hand, both fundamental and applied, are too varied to detail in this report, and information can be found in the valuable compilations and accounts of completed works which are now appearing in rapid succession in the Foundation's Technological and Scientific Report Series. Two novel and important reports are on the "Taste Sense, and Relative Sweetness of Sugars; etc."<sup>142</sup> and on "Sugars and Sugar Derivatives in Pharmacy."<sup>141</sup> Among the new 1948 publications announced,<sup>141</sup> but not yet to hand, are reports on Levulinic acid (Wiggins); Recovery of sucrose from molasses (Herndon); Allyl sucrose (Zief); Cacao and sugar (Weiss); Lead tetra-acetate as a tool for sugar research (Hockett *et al.*) and many others are in the press.

Notable results are coming from the medical and nutritional projects, from the baking studies and from the fundamental work at the M.I.T. Sugar Research Laboratory.

From other studies, allyl sucrose<sup>143</sup> has been shown to have a promising future in the coatings industry and pilot plant operations for the production of samples for evaluation by industry have begun. The Foundation's publications are emphasising the surprisingly diverse nature of the uses of sugar.

A valuable branch of the Foundation's activity is the compilation of a considerable library on the technology of sugar and on its historical phases and use. Investigators and students have ready accessibility to this library in New York. The Foundation has been fortunate in being able to acquire the library of the late Dr. Charles A. Browne.

With excellent foresight too, the Foundation has sponsored the publication in two volumes, of the complete researches to date of the great American carbohydrate chemist, Dr. C. S. Hudson.

In a private communication to the Reviewer, Dr. Hockett states that "glycerine production by fermentation is at last being developed for peace-time operation. A plant is being built in Matanzas, Cuba. The last link which made this development possible was large-scale diffusion separation of smaller from larger molecules. This process was a war-time project by the Sylvania Corporation, now part of American Viscose. A similar development may arise with lactic acid, which could command a large market in the plastics field if it could be made pure at a low cost competitive with all-synthetic processes.

Alcohol-injection devices are arousing definite interest as a means of obtaining high-octane gasoline performance from lower-octane gasoline. Petroleum interests will not oppose this development because engine design has so far outstripped productive capacity for high octane gas. All kinds of highly efficient engines have been tried and found excellent, but cannot be produced in quantity because their compression ratios (as high as 12 or 13 to 1) require very high octane gas. Consumers will approve this development because they can get better performance for less money. The use of such injectors is being tried out in key cities by taxi and bus companies. If every American car used the injector and burned 5% as much alcohol as gasoline a billion gallons of alcohol a year would be needed for this use alone—equivalent to 2,500,000,000 gallons of blackstrap—or five times the normal demand. This market could absorb all surplus blackstrap, a lot of synthetic methanol, alcohol from sulphite liquor, from surplus potatoes, and also from hydrolysis of cellulosic wastes.

Cane-wax recovery is being carried out on a moderate, semi-commercial scale in Cuba.

Furfural is still problematical though it is thought that research on recovery of both furfural and fibre might result in practical processes.

Liquid sugars are making gains in the United States, but nothing has been written on the subject.

Dextran is in use as a stabiliser with sugar syrups.

The general attitude in the industry toward ion-exchange processes is a degree of disillusionment following optimism, especially among beet processors. The verdict is that costs are too high for the benefits derived, but continuing research may still change this, especially considering by-product recovery. However, ion-exchange processes are in effective use for recovering sugar from waste pineapple juice, in Hawaii."

### **The work of the Colonial Products Research Council**

Steady progress continues on this project which was originated three years ago by Sir Norman Haworth at Birmingham. Recognition of the achievements has been made by the award to Dr. L. F. Wiggins, the leader of the research team, of the Harrison Medal and of the third of the valuable Awards of the Sugar Research Foundation. Dr. Wiggins has written an account<sup>144</sup> of his work on the utilisation of cane sugar for the production of chemicals useful in industry and medicine which summarises

the present position at this early stage. Substances marked for special attention are sucrose octa-acetate, mannitol, sorbitol; citric, tartaric, lactic, and levulinic acids; sulphonamide derivatives; anhydro sugars, and heterocyclics. Technological collaboration is now needed to evaluate some of the many promising chemicals for which synthetic methods have been made available. Dr. Wiggins has been appointed to the Directorship of Sugar Research and Technology at the Imperial College of Tropical Agriculture, but his team will continue to work for the next few years in the Reviewer's laboratories. Numerous papers from the group have appeared in the Journal of the Chemical Society for 1947 and 1948.

### General carbohydrate chemistry

Several useful books on fundamental carbohydrate chemistry have appeared. In particular, we have those of Pigman and Goepp,<sup>145</sup> and of Honeyman,<sup>146</sup> while a small monograph by McIlroy<sup>147</sup> on the polysaccharides has appeared, which includes useful information on analytical methods. Volume III (1948) of "Advances in Carbohydrate Chemistry"<sup>134</sup> continues to maintain the high standard of this publication. Of particular importance is C. S. Hudson's contribution on "Emil Fischer's Convention for Writing Stereochemical Formulae," and L. Sattler's chapter on the "Unfermentable Reducing Substances in Cane Molasses." Progress in the Chemistry of Carbohydrates has been reviewed<sup>148</sup> by D. A. Prins and R. W. Jeanloz, sugar alcohols, and deoxy sugars receiving special attention. The chemistry of the immuno-polysaccharides<sup>149</sup> has also been reviewed.

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# FOODS

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AN important development in many branches of science since the war has been the resumption of international congresses of scientists and the publishing of full reports of the proceedings. These contain many original contributions and reviews giving a picture of the state of knowledge up to date and the latest advances in a particular field. An outstanding example is the Official Report of the World's 8th Poultry Congress,<sup>1</sup> which met at Copenhagen in August, 1948. This contains material of interest to all poultry breeders and keepers and to producers of poultry products, ranging through nutrition and physiology, genetics, incubation, the organisation and development of the poultry industry, diseases and their control, the manufacture of egg products, marketing and poultry economics. Similarly, in Paris, in July, the 7th International Congress of the Agricultural Industries,<sup>2</sup> including many branches of the food industry, received contributions from most of the European countries and from Turkey, India, and the Americas.

Important, too, is Vol. 1 of "Advances in Food Research," published by the Academic Press Inc., N.Y., under the general editorship of Dr. E. M. Mrak of the University of California and Dr. G. F. Stewart of Iowa State College, assisted by an editorial board representative of several countries. The editors recognise that papers on food are scattered in innumerable journals and they offer "Advances in Food Research" as a contribution towards co-ordination and integration. The series is intended to cover all of what may be called food science, i.e., the whole body of scientific knowledge concerned with foods and their relationship to man. The editors divide food science into eight main fields: human nutrition (physiological and psychological factors affecting appetite), agriculture (cultural factors influencing acceptability and nutritive value), microbiology and public health, biochemistry and histology (composition and texture), food technology and engineering (processing, packaging, storage, etc.), entomology and zoology (insects and animals causing spoilage), and special considerations applying to individual commodities; Vol. 1 contains twelve copiously documented and authoritative articles falling within one or other of these areas.

## Meat and meat products

The fundamental knowledge of the physiological and biochemical properties of muscle has increased out of all recognition in the last two decades. It is now known<sup>4</sup> that glycogen is much more abundant in resting than in fatigued muscle and, since it is converted to lactic acid during rigor, the  $p_H$  of rested muscle will be low after rigor and that of fatigued muscle high—e.g., the flesh of farm-killed pigs will, on an

average, contain more lactic acid than factory killed pigs. Lactic acid is the natural preservative of meat; hence the flesh of rested animals resists bacterial attack and so keeps longer than that of fatigued animals. Low  $p_H$  increases the rate at which meat becomes tender during ripening, and also the rate of salt penetration, but it increases the drip after freezing and thawing or during cooking, although other factors play a part in these two cases. Most prominent among those who have helped to clarify this subject of the effect of fatigue during the year are Callow<sup>5</sup> and Ingram.<sup>6</sup> Callow<sup>7</sup> has also published Part 2 of his work "Comparative Studies of Meat," in which he has followed the changes during growth and fattening and their relation to the chemical composition of the fatty and muscular tissues, in the carcasses of twenty-nine cattle representing eight breeds, fifty-five sheep representing eight British breeds, and including a carcass from Iceland and one from Uruguay, and forty pigs of two breeds. The animals were of different ages and were killed at various stages from emaciation to fatness. This work has placed the grading of meat animals on a scientific basis.

Less comprehensive attempts to relate composition to quality were made in Germany during the war by Grau,<sup>8</sup> who determined the ratio of water to non-fatty organic solids [Feder number] in various beef joints of known history and origin and found that this generally increased as the quality of the meat decreased. Grau<sup>9</sup> also related the percentage of water to the calorific value of the meat, but Callow's finding that the yield of g.-calories from 100 g. of carcass of cattle or sheep is approximately ten times the percentage of fatty tissue would appear to be more useful.<sup>7</sup>

#### *Tests for quality of meat*

Tenderness in meat has been reviewed at length by Meara,<sup>10</sup> while Dearthage and Reimann<sup>11</sup> discussed the relative merits of organoleptic and mechanical methods for assessing it: in comparing beef steaks treated by the "Tenderay" process they found a trained tasting panel of six persons satisfactory. Low and Stewart<sup>12</sup> have also considered the factors involved in selecting subjective and objective tests for poultry meat and in choosing a panel of judges.

#### *Nutritive data: vitamins in meat*

Good retention of vitamins of the B-complex was found in beef after cooking by different methods, such loss as occurred being mainly collected in the drippings.<sup>13</sup> With pork, there are<sup>14</sup> considerable variations in the thiamin and riboflavin contents of different cuts from the same carcass: 90-93% of the thiamin of the cooked pork was retained after steaming, and even after steaming, cooling overnight, and reheating. With pork hams<sup>15</sup> the losses of B<sub>1</sub>, B<sub>2</sub>, and nicotinic acid were negligible during sweet-cure pickling, 8-15% during curing and smoking and 20% during boiling. Frozen storage had little or no effect in themselves, but predisposed the hams to increased loss during smoking. Livers and liver-pastes<sup>16</sup> from various domestic animals varied from being rich or moderate to rather poor (1500 to 64 i.u. per g. and 265 to 92 i.u. per g.). So far, it has not proved possible to determine vitamin B<sub>1</sub> or B<sub>2</sub> spectrophotometrically in yeast or meat extracts; hence biological and chemical methods of assay must still be relied on.<sup>17</sup>

*Meat products*

Journals published in Germany during the war and since are now receiving attention and, with sausages, the chief pre-occupations lay in preparing an acceptable product with various meat and vegetable mixtures. It is stated that soya sausages can now be produced which defy identification,<sup>20,21</sup> and methods of analysing these are given to ensure that nutritive values are maintained as far as possible.<sup>18-25</sup>

The preparation of fish and meat pastes of acceptable texture by the addition of cereal filler and biscuit crumbs is described by Burrell,<sup>26</sup> who also deals with the hygienic precautions necessary to prevent fermentative over-run.

*Whalemeat*

The meat shortage and the publicity given to the Antarctic factory whaling ship, *Balaena*, has stimulated interest in whalemeat, and an account of the Norwegian whaling industry in the North Atlantic, based on a visit to Norway, has been given by Ingram.<sup>27</sup> The whales are hunted about 100 miles out at sea and may either be cut up on board ship or towed to shore stations. Last year the Norwegians consumed about 5000 tons of whalemeat, the inferior grades being used to feed silver foxes. Much of the deterioration of whalemeat is due to inadequate bleeding and the slow cooling of the huge carcasses. Some improvement is effected by opening up the body cavity after death and allowing sea water to flow in and cool the tissues.

*Frozen meat*

Changes in colour from red to shades of brown, grey or black can occur on freezing and thawing bones containing red marrow, due to oxidation of haemoglobin to methaemoglobin.<sup>28</sup> The discoloration can spread to the tissues, but does not affect flavour and texture, and is minimised by cooking. Juiciness of the flesh of frozen fowls is not correlated with determinations of the bound and total water contents, but there appears to be a slight correlation between these and palatability.<sup>29</sup>

*Fish*

The advantages of freezing fish at very low temperatures as soon as possible after catching are now well known, and van den Broek<sup>30</sup> proposes deep freezing at  $-10$  to  $-35^{\circ}$  for Dutch trawlers instead of simple cooling to  $-1$  or  $-1.5^{\circ}$ . Banks<sup>31</sup> finds a loss of quality (denaturation of protein, rancidity, and desiccation) in a few weeks with fish stored at  $-9^{\circ}$  but, at  $-20^{\circ}$ , there is little or no deterioration in 2-4 months. He also discusses the possibility of freezing white fish at sea to avoid the staling which normally occurs. In the "Fairfree,"<sup>32</sup> an experimental trawler, fish is actually caught and frozen at  $-29^{\circ}$  and subsequently held at  $-23^{\circ}$ . It should be borne in mind that freshly defrosted fish differs little from fresh fish but deteriorates more rapidly; Costa and Cannella<sup>33</sup> report that rapid defrosting in water gives a more resistant product than slow defrosting in air.

Care in avoiding contamination with micro-organisms is a partial alternative to quick freezing fish and a large number of papers have been

published on the effect of contamination and the methods of avoiding it. Deterioration is judged *chemically* by determining the methylamine content and *organoleptically* by a tasting panel, the correlation between the two methods being good<sup>34</sup> although, unlike meat, fish does not improve by aging, even though it may have no spoilage tastes and odours. Castell<sup>35</sup> has shown that there is a definite relationship between the degree of microbial contamination and the keeping quality, a tenfold reduction in the bacterial count increasing the keeping time by approximately 1 day at 3.3°. He also showed<sup>36</sup> that, with unwashed fish, the count increased with time of storage on ice but, with plants which washed the fish immediately before filleting, there was a marked decrease when the filleting was done after four days on ice. Dyer<sup>37</sup> has classified the bacteria obtained from the slime and faeces of cod and found that 20% of them lysed fish muscle, 29% formed methylamine, 98% fermented carbohydrates, and 4% were chromogenic. Spoilage was entirely dependent on the extent of surface contamination during filleting.<sup>38</sup>

The relation of  $p_H$  to the freshness of fish has been studied by Elliott,<sup>39</sup> who finds that the surface  $p_H$  rises as spoilage progresses with haddocks, whiting and dabs. With other fish correlation is less satisfactory and is not dependable in thawed fish.

Castell and Anderson<sup>40</sup> have studied the effect of salting and smoking on the growth of *Clostridium* in fish. Ten per cent. of salt was necessary to prevent growth at 37°. Spores remained active for a year in fish muscle after salting and for a further 40 days after drying. Moderate smoking only destroyed vegetative forms.

Van den Broek<sup>41</sup> considers *bactericidal ice* less effective than 0.076%  $\text{NaNO}_2$  solution. Tarr<sup>42</sup> has also tested a large number of germicidal ices and found only four which delayed bacterial growth. In general they were most effective at low  $p_H$  (6.0–6.2). Tests with chlorine solutions, as preservatives of fish, showed that 1500 p.p.m. of available Cl did not affect the colour; 400 p.p.m. was easily detected and 200–300 p.p.m. could be detected by some tasters, but 200 p.p.m. did not improve the keeping quality.<sup>43</sup> Chlorine disinfectants can be useful, however, for disinfection in and around fish plants and Castell<sup>44</sup> suggests the quantities in p.p.m. of available Cl which should be used for various items of equipment.

In studies on the control of rancidity in fish Tarr<sup>45</sup> notes that little trouble occurs at  $-28^\circ$ , but it develops rapidly at  $-10^\circ$  and can be considerably retarded by several anti-oxidants. Two of the substances tried also prevented the bleaching of salmon.

Dyer and Dyer<sup>46</sup> have drawn attention to the leaching from fish of soluble proteins, amino acids, and other nutrients, responsible for flavour, through packing with melting ice in uninsulated holds or in warm sheds ashore. The deterioration in quality which ensues can be avoided by cooling the fish quickly and maintaining it as near the freezing point as possible. In studies of the sulphur-distribution in fish proteins Beveridge<sup>47</sup> has recorded the presence of cystine and states that, apart from ovalbumin, crude fish protein is the best source of *methionine*.

Shell fish tend to be neglected, but the correct conditions for successful clam-farming have been determined in Nova Scotia.<sup>48</sup> The digging and

planting of "seed" is described and three years is required for the clams to attain marketable size.

### Milk and milk products

As usual, a great many papers on all aspects of dairying and dairy produce have been published but, many of the more important aspects of this work are brought together in the Milk Section of the Report of the XIth International Congress of Pure and Applied Chemistry.

#### *Liquid milk*

An American Committee on Milk and Dairy Products<sup>49</sup> has considered the influence of factors like methods of handling, production, distribution, and use on the food value of milk. Neither the riboflavin nor the thiamin content of the milk is affected by the type of food eaten by the cow, but the vitamin A content depends directly on the carotene in the cows' diet and remains stable in handling and processing.

The working of the present statutory methylene blue test with several thousand samples of pasteurised milk in London, over a one-year period, has been examined and compared with other standard tests by Davis and Watson.<sup>50</sup> Mitchell and Frary<sup>51</sup> have examined three serum methods for determining added water in milk. The Cu serum method is the most rapid; the cryoscopic method is also rapid and is the more reliable. For detecting skim milk, as an adulterant of whole milk, Weinstein<sup>52</sup> recommends the Helkma-Trypan blue reaction as being capable of indicating a 10% adulteration, and Schwarz and Fischer<sup>53</sup> claim to detect by a modified Scharrer method, the addition of 2% of raw milk to pasteurised milk, and also a failure by 2° to heat milk to the prescribed temperature. Physical instability of milk, normal in other respects, is attributed by Seekles<sup>54</sup> to increased Ca<sup>++</sup> activity. Normal milk can be made unstable by adding CaCl<sub>2</sub> and restoring the  $p_H$  to its original value with NaOH. It is considered that instability may be due to conditions in cattle causing disturbance of the mineral balance. Cows producing abnormal milk were often successfully treated by oral or subcutaneous administration of sodium citrate. In pasteurised milk, failure of stabilisation has been related to the presence of oxygen leading to a reduction in acidity, a decrease in the solubility of Ca phosphates and the development of sporulating organisms which produce rennin.<sup>55</sup>

#### *Cream*

The influence of the mechanical treatment of milk and cream on the size and distribution of the fat globules has been investigated by Lyons,<sup>56</sup> using a beater-type flash heater to bring the milk to separating temperature. Mohr and Wellm<sup>57</sup> and Mohr and Kiel<sup>58</sup> give data regarding the viscosity of concentrated cream, and the deformation of the fat globules which occurs when more than 70% of the cream is fat, and they also discuss the theory of the stability of fat.

The deterioration, on storage, of dried skim milk has been attributed largely to a Maillard reaction between the free amino groups of the protein and lactose, leading to losses of palatability, solubility, colour, and the biological value of the protein.<sup>59-61</sup> [The Maillard, or the non-enzymic browning reaction, is important with several classes of foods

and has been discussed with eggs, potato, and fruit.<sup>62]</sup> Canadian workers report<sup>63</sup> a seasonal change in the palatability and keeping quality of skim milk powder. The storage life of whole-milk powder is considerably lengthened by preheating the milk before drying, 88° giving better results than 71°. <sup>64</sup> The biological value and true digestibility was only slightly lessened by heating to the higher temperature.<sup>65</sup>

New Zealand cheeses, stored up to three months in an insulated room at 12.8° and R.H. 80–82%, were of better quality and suffered less shrinkage than cheeses stored without control of temperature and humidity.<sup>66</sup> Numerous breakdown products in blue mould cheese have been isolated and identified,<sup>67</sup> but attempts to relate the flavour of cheese to fatty acids, soluble proteins,  $p_H$ , moisture, salt content, volatiles, etc., gave mostly negative results.<sup>68</sup>

In the ripening of Camembert cheese there are a succession of predominating diplococci,<sup>69</sup> and, in using multiple-strain starters, one strain may overgrow the others and become responsible for most of the acid production.<sup>70</sup> Elimination of a predominant strain by a phage usually allows another strain to take over acid production and so restore the acid-producing properties of the starter. Starters may be infected from whey in milk cans.<sup>71</sup>

The colloidal behaviour, behaviour on decomposition, particle size, etc., are discussed at length by Kunzel and Doehner<sup>72</sup> in 1940, in a paper which has recently received notice in this country. Peters and Nelson<sup>73</sup> have attempted, with promising results,<sup>74</sup> to produce a good yield of microbial lipase from *Mycotorula lipolytica* to replace milk lipase in the production of cheese (Roquefort-type) from pasteurised milk, and Liebich<sup>75</sup> has prepared a combination of yeast and milk proteins which is said to be equal to animal proteins in food value.

### Butter and edible fats

Some theoretical aspects of the "New Way" butter process are described by Hill.<sup>76</sup> Pasteurised cream is shock-cooled to 60° F. and concentrated to 80% fat content. It is then drawn into a vat without agitation, standardised to the correct water and salt content, cooled rapidly to low temperature, and the type of emulsion changed in an extruder where the fat solidifies. The advantages of the method and its effect on the composition of the butter are discussed. The continuous Swiss butter-making process, in which CO<sub>2</sub> under pressure replaces lactic acid and promotes the rapid formation of butter granules, is also described by Stussi.<sup>77</sup>

Comprehensive studies on the storage of salted butter at 30°, 50°, 70° and 90° F. have been carried out in Canada.<sup>78</sup> Deterioration was assessed by flavour score and by chemical and microbiological tests. The total serum acidity,  $p_H$ , and serum fluorescence were the factors associated most closely with the flavour score.

The all-the-year-round grazing of cattle in New Zealand results, according to Barnicoat,<sup>79</sup> in an increase in the vitamin A potency of butterfat from about 35 i.u. per g. in late summer to about 47 i.u. per g. in late winter and spring. This is the exact opposite to what happens in Europe.

The *aroma and flavour of butter* are of perennial interest : Carlinfanti<sup>80</sup> regards glucose as the parent substance and citric acid as a H-acceptor in the bacterial production of the diacetyl and acetone, responsible for aroma. Peterson<sup>81</sup> summarises recent progress in Sweden, Denmark, and Finland in preventing the development of oily and fishy tastes. He concludes that it is most important to use sweet cream and to control  $p_H$  at 6.0-7.0. Oxidation reactions are slower in unwashed than in washed butter. Special salting and anti-oxidants reduce oiliness, but they prevent the production of first-grade butter. Metallic and metallic oily flavours in sour cream, and the butter made from it, are said to be caused by the oxidation of the fat or fat-like constituents.<sup>82</sup> They increase with acidity and can be prevented by anti-oxidants; hence the oxidation probably occurs either at the boundary of the fat-phase or in the water phase. According to Mulder and Kleikamp<sup>83</sup> milk salts are partly responsible since these flavour defects are absent in washed cream.

Mohr<sup>84</sup> has devised tests for and discusses the "oiling off" of butter and finds that butters produced by the Fritz and Alpha processes "oil off" more than churned butters. Mohr and Hennings<sup>85</sup> also describe apparatus and procedures for determining the dielectric constant for butter. This varies between 5.0 and 7.5 according to the state and degree of emulsification and the air and water contents. It is suggested that these measurements could be useful in the control of continuous butter-making plants.

### *Edible fats*

In the field of fats generally, a comparatively simple method for the estimation of linoleic acid promises to be of value to the food chemist (Stainsby, W. J., *Analyst* 1948, **73**, 429). Of some interest also in this time of fat shortage is the review by Kleinzeller<sup>86</sup> on the synthesis of lipides, particularly by micro-organisms. Much interest is also being shown in the various processes of solvent segregation and inter-esterification whereby the physical and chemical properties of natural fats can be altered to fit our needs more closely.<sup>87</sup> Further evidence in support of Farmer's radical chain theory of the auto-oxidative deterioration of fats has been produced by Bickford<sup>88</sup> *et al.*, and some of the reactions of methyl oleate hydroperoxide have been investigated,<sup>89</sup> certain of the decomposition products being identified.<sup>90</sup> There is also a useful review on lipoxidase and the auto-oxidation of unsaturated fatty acids by Bergström and Holman,<sup>91</sup> and much interest continues to be shown in the phenomenon of "reversion" in the soya bean and similar linolenic-glyceride-containing oils : Martin *et al.*<sup>92</sup> have succeeded in isolating  $\alpha$ -heptenal from reverted soya bean oil.

The chief developments in the manufacture of *margarine* during the last 20 years are discussed by Arup,<sup>93</sup> while Schär has reported, for a Swiss Food Commission, on the activity of specialists in the edible fats and oils division of the Swiss society of analytical and applied chemistry.

### *Eggs*

With shell eggs interest is now centred on the effect of *oiling* in prolonging the storage life and preventing the enlargement of the air space.

Gibbons *et al.*<sup>95</sup> find that oiled eggs maintain their grades two to three times longer than untreated eggs and lose about one-tenth to one-quarter as much weight. Wendland,<sup>96</sup> however, recommends dipping eggs for 1 min. in 0.5 to 1.0%  $H_2SO_4$  followed by 1 min. in 1 to 2% water-glass. This forms a firm layer of  $CaSO_4$  and  $CaSiO_3$  on the shell which prevents both the entry of micro-organisms and loss of water.

Kaess<sup>97</sup> compares the result of oiling with various proprietary preparations with storage in saturated lime-water. He claims that the addition of 0.6% of NaCl to the lime-water to some extent prevents the thinning of the white.

Winter *et al.*<sup>98</sup> destroyed coliform bacteria in samples of commercial liquid and frozen whole egg by *pasteurising* at 146° F. for 0.5 min., 144° F. for 1 min., 142° F. for 1.5 min., and 140° F. for 2.5 min. The effect of heating on the functional properties of liquid egg albumen is discussed by Hosberg,<sup>99</sup> who noticed that the foaming capacity of fresh egg-white is destroyed or diminished by heating at 120° F. for 1 hour, or at higher temperatures for shorter times. Stability towards heat is improved by reducing the  $p_H$  from 8.5 to 7.0 or 6.0 and also by adding sugars.

A considerable number of papers have appeared on *dried egg*, some of which, no doubt, are reports of work carried out during the war, and are chiefly concerned with its microbiology and keeping properties. Gibbons<sup>100</sup> has isolated fourteen types of *Salmonella* organisms from 28% of samples of dried egg examined during 1945, and *S. pullorum* from 4%. In most samples, the probable number of organisms was less than 1 per g. Solowey *et al.*<sup>101</sup> examined altogether 5198 samples of dried egg from 100 plants and claim to have isolated as many as 52 types of *Salmonellae*. Solowey<sup>102</sup> also states that the ratio of paracolon organisms to *Salmonellae* was as 1 to 10.

McFarlane *et al.*<sup>103</sup> noticed low microbial counts with dried egg in periods of high shell production when mostly fresh eggs are dried: stored frozen eggs give high counts. Sutton and McFarlane<sup>104</sup> isolated *Escherichia coli* from about 1% of spray-dried whole egg samples containing 4–6% of moisture. Hirschmann and Lightbody<sup>105</sup> inoculated liquid and dried egg with *Pseudomonas fluorescens* and related the deterioration, as estimated by changes in lipid fluorescence, free fatty acid content,  $p_H$ , palatability, and resazurin colour, either to the activity of these bacteria, unaccompanied by reproduction, or to cell components, presumably enzymes, that remain active after the death of the organisms.<sup>106</sup>

Canadian workers<sup>107–109</sup> report the results of adding a large number of different substances to whole egg powder. They advocate the addition of artificial colour to Canadian dried egg to suit the English market and also describe the preparation of dried egg from frozen egg pulp.

Makower and Shaw<sup>110</sup> studied the absorption of oxygen by dried egg and its relation to light intensity and water content.

### Cereals and cereal products

Scientific progress in the baking industry during 1947 has been well reviewed by Butterworth,<sup>111</sup> who refers to progress in the organisation

of research and technical training and comments usefully on current bakery and cereal literature.

In order to mill flour and obtain the best nutritional value, colour, and baking properties a complete series of sixteen fractions of Dutch-grown wheat were subjected to detailed chemical analysis under the Netherlands Broodgraan-en Broodcommissie.<sup>112</sup> Improved methods of analysis were developed and, by making certain assumptions, an equation was derived by which the morphological composition of a series of fractions could be calculated from a knowledge of the raw fibre,  $\text{PO}_4'''$ , and starch contents. As the rate of extraction rose above 77.6% the percentage of substances of nutritional value and also of phytin rose, a finding which was in agreement with a similar but more limited test in America. The baking quality of the flour decreased noticeably as the rate of extraction exceeded 81% and it was considered that an extraction rate of 80% should fulfil all reasonable requirements.

Three methods of determining the extraction rate in flours are reported by Von Fellenberg,<sup>113</sup> the most sensitive being based on staining the flour with phloroglucinol and HCl after treatment with glacial acetic acid and HCl. Lignin particles, derived from the bran, are coloured red, and the colour matched with that of a powder of known lignin content.

There has been much controversy about the treatment of flour (bleaching) and the matter is still under investigation, although there is no evidence that it is harmful to man.<sup>114</sup> So-called "enrichment" has also been criticised: Beaty and Fairbanks<sup>115</sup> fed female rats during the gestation-lactation period with six different types of bread in *ad lib.* experiments over three successive litters. White flour bread supplemented with 6% of non-fatty dry milk solids was superior to unsupplemented white flour bread and also to wholemeal bread with and without non-fatty milk. Bread "enriched" with vitamin B<sub>1</sub>, riboflavin, nicotinic acid, and Fe to the U.S. Federal Register Standards was not significantly different from similar non-enriched bread. Wholemeal bread was inferior to all other types; in fact, on this bread, rats failed to wean any young in the third litter. It is not known how far the gestation-lactation period is representative of other periods of life, but the results are striking and strengthen the position of those who believe that bread could best be improved by adding fat and milk products.<sup>111</sup>

Attempts to relate the thiamin content of wheat to weather, variety, location, and season are recorded by O'Donnell and Bayfield,<sup>116</sup> but, in any case, the thiamin content of wheat is not related to that of the flour milled from it.

The effects of  $\alpha$ - and  $\beta$ -amylase in bread making have received attention, and Selman and Summer (Cereal Chemistry 1947, 24, 207) have compared the results given by the amylograph with those obtained from gassing tests and maltose tests. Cunliffe<sup>117</sup> has examined the possible relationship between the dextrin figure in bread and crumb-stickiness. He considers that flours with a dextrin figure > 13.0 will almost certainly produce bread with a sticky crumb.

Several papers have appeared<sup>118</sup> on the nature,<sup>119</sup> retardation, and measurement of bread staling: Schoch and French<sup>120</sup> consider that amylose takes no part in this process and that staling may be due to

a spontaneous aggregation of amylopectin, the predominant ingredient of the water-soluble starch of bread. Favor and Johnston<sup>121</sup> found that poly-oxyethylene stearate, in quantities up to 2% of the flour weight, markedly retarded the toughening of bread crumb with age, but had no other significant effect on the dough or bread.

The formation of a protein lipid complex during dough mixing is reported by Olcott and Mechem,<sup>122</sup> and Zeleny<sup>123</sup> has found a close correlation between loaf volume and the volume of solid material deposited in a sedimentation test with dilute lactic acid. The test can be used to estimate the gluten value of bread-making flours.

Johnson and Miller,<sup>124</sup> working with malt supplements, have found fungal amylases much more active in producing sticky doughs than ordinary malted wheat amylase, and Walker<sup>125</sup> has studied the effect of different methods of baking on the phytate-phosphorus content of bread. In rye bread 72% of the phytin is said to be decomposed in leavening, the amount remaining being insufficient to interfere with Ca metabolism.<sup>126</sup> It is claimed that by dielectric heating to 150° rye can be made equal to wheat for baking purposes.<sup>127</sup>

Rice milling, and particularly the advantages of parboiling before milling on the retention of thiamin and on the general quality of the product, are dealt with in several papers.<sup>128-130</sup>

As regards equipment in the bakery, Bailey<sup>131</sup> states that the use of aluminium tins and sheets gives more even baking and thus improves the appearance of bread, cakes, and Swiss rolls.

## Fruits and vegetables

Research on fruits has been chiefly concerned either with storage under various conditions above freezing (cool-storage) or with preservation by freezing. The conditions necessary for the short-term (4-10 days) cool-storage of the most important fruits and vegetables have been defined by Fidler in a leaflet<sup>132</sup> intended primarily as a guide for wholesalers and retailers. For long-term cool-storage the cooling effect is often reinforced by atmosphere control (refrigerated gas-storage), by coatings or wrappings applied to the fruit or by exposing it to traces of volatile substances possessing fungicidal or other preservative properties. The response to these measures of different kinds of fruit, different varieties of the same fruit or even of the same variety at different stages of development or in different seasons can vary considerably. What is beneficial in one case may cause injury—scald, low temperature breakdown or abnormality, internal browning (brown heart)—in another. Hence there is endless scope for observing the effect of modifying existing methods and trying new ones and, in no branch of research is it more necessary to repeat results before drawing conclusions.

### *Cool-storage of fruit*

In tests carried out over two seasons, W. H. Smith<sup>133</sup> completely controlled the internal browning of Victoria plums, which normally occurs after storage at 0-5°, by warming them up to 18° for two days during a critical period between the 15th and 20th days from the start of storage. The plums, which were divided into two lots, half-red

(firm-ripe) and less than half-red initially, were stored for 40 days altogether and subsequently ripened normally and with very little browning in 2 to 4 days at  $18^{\circ}$ , although plums of the riper group were preferable to those of the less ripe. After 51 days in store internal browning was more severe, especially in the immature group. Fisher, Button, and O'Reilly,<sup>134</sup> in U.S.A., studied the effects of storage temperature, harvesting conditions, and pre-ripening on the storage life of seven varieties of peaches. Varietal and seasonal differences were noticed and at  $15.5^{\circ}$  to  $26.6^{\circ}$ , during ripening in the packing house, there was a rapid hydrolysis of pectose to soluble pectin and the respiration rate reached a maximum about 24 hours after picking. These changes were much less evident at  $0^{\circ}$ , but the storage life was not prolonged by introducing 7-9% of  $\text{CO}_2$  into the atmosphere. Better results were obtained with less  $\text{CO}_2$  (2 to 5%) and  $0^{\circ}$  was preferable to  $4.4^{\circ}$  as a storage temperature.<sup>135</sup> Two to 5 days' exposure to  $23.9^{\circ}$  after picking and before cool-storage prevented meakiness.

Claypool and Allen<sup>136</sup> have varied the storage atmospheres at  $4.4^{\circ}$  and  $18^{\circ}$  (ripening temperature) with plums, pears, peaches, and grapes in tests designed to improve transport conditions: extended storage life and subsequent normal ripening were achieved in several cases. Similar tests have also been carried out with apples.<sup>137,138</sup>

Success has been claimed<sup>139</sup> in controlling scald in apples during two successive seasons by exposing them, in cool-storage at  $0^{\circ}$  for the first five days after harvesting, to air containing a high concentration of carbon dioxide. In 1944, three days in 30% of  $\text{CO}_2$  was effective but, in 1945 (a bad year for scald) 5 days in 50%  $\text{CO}_2$  were required. The treatment delayed ripening and lengthened storage-life and, although two varieties showed slight injury, nine were uninjured.

The search for new substances which can be applied to fruits, either by spraying or dipping, in order to prolong their storage-life still goes on.<sup>140,141</sup> Many of these are of a waxy or oily nature or may even be solutions containing rubber. They act by preventing shrinkage through evaporation and by retarding respiration and fungal attack, each fruit being, in effect, converted into a miniature gas store.

Non-waxy dips, said to be effective in reducing fungal rotting in oranges, were 5% Ag thioacetamide, 8-hydroxyquinoline, and 2-aminothiazole,<sup>142</sup> while pear-scald was controlled by dipping in carbowax containing 50 p.p.m. of 2:4-dichlorophenoxy acetic acid, wrapping in paper and storing at  $-0.5^{\circ}$ .<sup>143</sup> With grapes, considerable benefit is reported through packing with bentonite.<sup>144</sup>

### *Freezing fruits and vegetables*

A revised edition of Food Investigation Leaflet No. 2 of the Department of Scientific and Industrial Research by Morris, Barker, and Gane<sup>145</sup> describes the conditions to be aimed at in preserving fruits and vegetables by freezing, and gives data and practical directions useful to processors. In U.S.A. Schrader and Scott<sup>146</sup> have classified strawberries according to their ability to retain their colour, flavour and texture after quick-freezing at  $-28.9^{\circ}$  to  $-23.2^{\circ}$ , followed by storage at  $-17.8^{\circ}$  but, in work carried out over two seasons, it was concluded by other workers<sup>147</sup> that no chemical

relation exists between the suitability for freezing and any of the chemical constituents studied. Great varietal differences were observed in  $p_H$ , free acidity, ascorbic acid content, soluble solids and colour, and there were seasonal variations within each variety; for instance, the ascorbic acid content varied from 50 to 90 mg. per 100 g. A similar variation in ascorbic acid was found by Scott and Schrader,<sup>148</sup> viz., about 20% in storage at 0° for 4 months, the loss being proportionately greatest in samples with a high initial ascorbic acid content. Similarly, the high ascorbic acid content of pulped frozen guava falls rapidly, one-third being lost in the first month, after which the rate of loss decreases.<sup>149</sup>

Hills, Nevin, and Heller<sup>150</sup> have "firmed" apple slices with  $\text{CaCl}_2$  and other Ca salts by several different techniques, that most favoured being to soak the slices for 5 mins. in a 0.2% solution of  $\text{CaCl}_2$  after blanching for 90 seconds. The quantity of  $\text{CaCl}_2$  necessary for firming is stated to be too small to affect flavour. Other workers<sup>151,152</sup> have dipped apple slices in solutions containing  $\text{SO}_2$ , NaCl, ascorbic, citric or phosphoric acids either alone or in combination to prevent browning: 0.1% of  $\text{CaCl}_2$  may be added to the dip to give a firming effect.

Cass<sup>153</sup> has described the chief varieties of dates, their properties, world production, and the processes involved in manufacturing date flour.

Seasonal changes in oranges, grapefruit, and tangerines from the point-of-view of consumer acceptance are described by Harding<sup>154</sup> in terms of total soluble solids, total acid, and the ratio, solids : acid. As might be expected, the acid content falls rapidly during ripening.

### Fruit juices

Traces of copper in tomato juice, sufficient to cause loss of ascorbic acid, may be derived from copper sprays, which adhere to the fruit and are not completely removed by washing and peeling. The amount of the loss during the processing of the juice increases with the copper content but, in storage after canning, the copper becomes deposited on the tin and ceases to have any effect.<sup>155</sup> Pre-sterilising is said to reduce the incidence of "flat-sours"<sup>156</sup> and the whole subject of canning tomato juice, with descriptions of varieties and standard tests for the presence of insect fragments and mould hyphae has been reviewed by Cruess.<sup>157</sup>

The use of ion-exchange resins opens up new possibilities in separating the soluble constituents of biological liquids like fruit juices and Hadorn<sup>158</sup> and Gore<sup>159</sup> have described the use of these for preparing clear, bland syrups and concentrates from fruit juices, while Buck and Mottern<sup>160</sup> have prepared *l*-malic acid by regenerating the exchanger with  $\text{Na}_2\text{CO}_3$  solution, concentrating the washings to 20% of sodium malate, precipitating at  $p_H$  6 as the Ca salt with  $\text{CaCl}_2$  solution, and treating the precipitate with 50%  $\text{H}_2\text{SO}_4$ .

Ascorbic acid continues to be advocated for preventing the enzymic browning of fruits such as apples, although reports as to its efficacy are not unanimous. Pederson<sup>161</sup> claims benefit from spraying apples, during or immediately after milling for juice extraction with a solution of ascorbic acid in apple juice. The extracted juice is then processed as usual and stored at a temperature below 21°. It is also claimed<sup>162</sup> that the addition

of ascorbic acid inhibits the formation of a musty flavour in apple juice preserved by freezing.

The off-flavour which develops in processed orange juice is ascribed by Curl and Veldhuis<sup>163</sup> to the lipin or fatty fraction in the suspended material and not peel-oil as is often supposed. Filtration removes these fractions but causes loss of flavour and aroma as also, according to Blumenkranz,<sup>164</sup> does exposure to light of  $\lambda < 4900 \text{ \AA}$ .

Useful data on the quantities of ascorbic acid in grapefruit and orange juices, and their blends, before and after storage for different periods at room temperature are given by Sale *et al.*<sup>165</sup> Attempts to produce fruit juice concentrates and powders by vacuum methods still go on, and Schroeder and Cotton<sup>166</sup> and Schwartz and Penn<sup>167</sup> claim good results with orange juice. Some loss of flavour is unavoidable, however, by these methods, and the powders are extremely hygroscopic. The only satisfactory method of concentrating fruit juices from the point of view of preserving the flavour, is by freezing and removing the water, as ice, from a liquid phase containing all the solutes. Considering that this process has been mooted, since about 1914, it is surprising that it has not been more widely applied. It was used on a large scale for onion and other juices in Germany during the war and Lee, Beattie, and Pederson<sup>168</sup> have now applied it to concentrate onion juice experimentally to 56° Brix in U.S.A. It has also been the subject of U.S.P. 2,436,218, 17.2.48, and Gane<sup>169</sup> has given details of the experimental procedure for concentrating fruit juices, vinegars, ciders, and stout by freezing, together with data likely to be useful in carrying out the process on a manufacturing scale.

## Vegetables

With dehydrated vegetables the moisture content is a major factor influencing the keeping quality. Tomato products are comparatively easy to dry by the Sardik process in the form of tomato flakes but, even when stored under nitrogen, these should not contain more than 3½% of moisture at 4.5° and 1½ to 2½% (preferably, the former) at room temperature. At 38° there should not be more than 1% of water and, even so, 33% of the ascorbic acid may be lost within 32 weeks.<sup>170</sup>

In preparing vegetables for canning, freezing, or drying more vitamins and minerals are retained in scalding (blanching) at a high temperature for a short time than at a low temperature for a long time.<sup>171-173</sup> Blackening during scalding, owing to the presence of iron, may be prevented by adding 0.2-0.4% of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  to the scalding water.<sup>174</sup> The electronic blanching of vegetables inactivates undesirable enzymes and causes no loss of soluble solids but leads to very high losses of ascorbic acid.<sup>175,176</sup>

That mincing or chopping vegetables can cause loss of ascorbic acid is well known, and the proportions of reversibly oxidised ascorbic acid, dehydroascorbic acid and residual ascorbic acid in chopped cabbage have been determined.<sup>177</sup> Loss has also been demonstrated with green peppers, radish, onions, cucumbers, lettuce, tomatoes, and cabbage,<sup>178</sup> both during mincing and subsequently, and the use of blades made of

plastic composition rather than steel for mincing is said to have been beneficial.

Bedford and McGregor<sup>179</sup> determined the changes in the proportions of ascorbic and dehydroascorbic acids during frozen storage and subsequent cooking, as well as in scalding, chard, spinach, peas, and snap and Lima beans. In the fresh vegetables dehydroascorbic acid formed 5–16% of the total. After scalding it decreased to 3–12% but increased to 24–94% during frozen storage and was reduced again to 15–44% during cooking. Patton and Miller<sup>180</sup> state that the storage of fresh vegetables with crushed ice favours the retentions of vitamin C as well as preventing loss in weight.

Brown<sup>181</sup> noticed that the carotene content of growing carrots increased with maturity up to 100 days after sowing and thereafter fell slightly but increased again during 30 days of storage and then remained constant for 30 days.

Differences in the hardness of harvested peas after cooking has long been a problem, and Mattson<sup>182</sup> reports that it depends mainly on the relation between the phytin and pectin and on the nature of the cations. Peas containing excess of Ca and Mg do not soften readily, but can be improved by adding suitable anions, *e.g.*,  $\text{PO}_4'''$  or  $\text{CO}_3''$ . In some samples sufficient phytin is present to precipitate the Ca and Mg and permit softening but, if the peas are soaked too long in water, the phytin is decomposed by phytase; hence the Ca and Mg are not precipitated and the peas remain hard on cooking. Moreover, phytin cannot precipitate Ca and Mg at  $p_H$  4–5 but at higher  $p_H$  values precipitation is almost complete.

Baumgartner<sup>183</sup> has described the curing of vegetables for pickle manufacture and, in a series of articles, Burrell<sup>184</sup> has also dealt with this subject, discussing its microbiology and proceeding to deal with the large-scale pickling of onions, cucumbers, and cauliflowers, and the methods for manufacturing piccalilli, pickled cabbage, mushroom ketchup, sweet pickles, chutneys, etc., giving typical formulae.

A notable contribution to literature on food is "The Potato, a comprehensive survey of its history and of the factors influencing its yield, nutritive value, and storage," by W. G. Burton.\* The book, which is well illustrated and indexed, also contains an account of the preparation and storage of the principal potato products.

The development of solanine in potatoes has been studied by Lepper,<sup>185</sup> who states that considerable quantities were found in potatoes stored in a dark cellar but, contrary to expectations, another crop, which had been exposed to light and become green, contained less. The type of manure used did not affect this result. According to Chao-yu,<sup>186</sup> however, Chinese cabbage manured with night-soil contains more available protein than cabbage manured with ordinary fertilisers—a result which will please the "organic farming" enthusiasts.

### Processed foods: cured, canned, dehydrated, and frozen

Of interest to all food processors and other users of aluminium equipment is Food Investigation Special Report No. 50, Department of

\* Chapman and Hall, London, 1948, 319 pp.

Scientific and Industrial Research, "Aluminium and Aluminium Alloys in the Food Industry," by J. M. Bryan, which is a comprehensive and fully documented account of the behaviour of aluminium and its alloys towards acids, alkalies, water, dissolved salts and all classes of foods, under conditions likely to be met with in the factory. The influence of the physical condition and composition of the metal and its surface-film of oxide on its corrodibility, and the methods by which corrosion can be prevented or checked are fully discussed.

A series of papers<sup>187-189</sup> on Canadian Wiltshire bacon deals with the increases in saltiness observed during the initial stages of storing, with losses of aneurin, riboflavin, and niacin in cooking pork and during curing and storage; and with the reduction of these losses which would result from "rebuilding" spent pickle.

In canning, a general review of the growth of the canning industry in this country and of the research facilities and progress at Chipping Campden have been given by Hirst.<sup>190</sup> Adam<sup>191</sup> gives three examples of the use of statistical methods in research on food-canning and discusses the value of these methods in planning research and interpreting results. The paper follows one by Finney<sup>192</sup> on statistical methods as applied to food problems generally.

Current trends in nutrition research on canned foods are reviewed by Pilcher and Clark,<sup>193</sup> who indicate that interest is now being taken in the effect on the retention of vitamins of the type of canning process employed. They instance the improved control of heat-resisting organisms by a preliminary sterilisation of tomato juice, vegetable purées, strained foods, and dairy products before filling into cans. This does not affect the content of aneurin (thiamin) and niacin in the final product. The nutritive value of canned foods is, in fact, the subject of numerous papers: Kramer<sup>194</sup> gives tables for the water, protein, fat, fibre, ash, carbohydrate, Ca, P, and Fe contents of a large number of canned foods. Others are concerned with the retention of vitamins *A*, *B*<sub>1</sub>, and *D* in canned fish<sup>195</sup>; of thiamin, riboflavin, and niacin in canned asparagus, green beans, peas, and Lima beans<sup>196</sup>; the retention of thiamin and ascorbic acid in raw and canned peas,<sup>197</sup> and in various other fruits and vegetables<sup>198</sup>; and with the effect of time and temperature of storage on the vitamin content of commercially canned fruits and fruit juices.<sup>199</sup> At ordinary room temperatures (50-65° F.) there was generally little or no loss of ascorbic acid, carotene, thiamin, and riboflavin, and only slight loss of niacin (in tomatoes) in a year but, at 80°, there were definite losses.

A mathematical treatment of the theory of heat sterilisation in canned foods is given by Riedel,<sup>200</sup> and an interesting series of papers has appeared<sup>201-206</sup> on thermal processing, chiefly of canned meat and bacon. The subjects dealt with are the dormancy of spores, which was most evident after processing at temperatures approaching destruction; the effect of various anions; and the thermal resistance of organisms after different treatments. It was recommended that processing should be based on the most resistant organism likely to be present.

Ulrich and Halvorson<sup>207</sup> have examined the bacterial population of canned bacon, produced during the incubation of samples at 37.8°, and

found that, in general, the less water present the lower the bacterial population.

Bashford<sup>208</sup> has confirmed previous observations that there is a correlation between the bacterial count of cooling water for cans and the number of blown cans. He proposes as a variant of a well known test for the efficiency of sealing compounds to subject cans to standard mechanical damage and immerse them in water containing a large amount of *Aerobacter aerogenes*.

Schormüller<sup>209</sup> has discussed the corrosion of black plate, tinplate, and aluminium containers and given a comprehensive review of information on the stability of vitamins in various containers, and Hollett<sup>210</sup> has related a metallic odour and flavour in canned herring to corrosion of the steel base of the cans.

As regards the actual canning of commodities, two papers<sup>211-212</sup> deal with the addition of  $\text{CaCl}_2$  in canning apples to increase the firmness of the slices. (see also 48-50) Culpepper *et al.*<sup>213</sup> describe the canning of sweet peppers to obtain a product rich in ascorbic acid; Cruess<sup>214</sup> gives a picture of the canning of asparagus in California, including methods of growth and harvesting, and MacDougall and Gibbons<sup>215</sup> have examined the effect of the method of pre-cooking on the weight of meat to add in canning poultry in order to obtain a product containing the 50% of solid meat required by Canadian regulations in a jellied pack. Contrary to expectations, based on losses in weight during pre-cooking, a slightly greater amount of meat, cooked in an open kettle, than of pressure cooked meat is required.

In Food Investigation Special Report No. 53\* of the Department of Scientific and Industrial Research, Ede and Hales<sup>216</sup> have recorded observations of the actual course of *drying* fruits and vegetables in specially constructed hot-air driers in which both the wet and dry bulb temperatures and the air speeds could be accurately controlled. They have thus accumulated fundamental data essential to the practical working of full-scale driers and have also indicated the optimum conditions from the point of view of the products concerned.

The public health aspect of dehydrated foods is dealt with in a report of a U.S.A. Committee on Foods.<sup>217</sup> Neither dysentery nor *Cl. botulinum* were found in any dried foods, but *Salmonellae* and staphylococci were demonstrated, particularly in dried egg. Dehydrated vegetables contained a considerable bacterial flora and their ascorbic acid and thiamin contents were reduced. Generally speaking, dried vegetables, meat, fish, and eggs should be cooked as soon as possible after reconstitution.

Damage during drying, particularly as applied to lucerne, is discussed by Zimmermann,<sup>218</sup> and a communal grass-drying experiment by Tutton.<sup>219</sup> With lucerne, the damage increased both with temperature and time of drying, but the digestibility of the proteins, etc., was reduced to less than their biological value. A new type of metabolism cage for animals is described.

Whitmore *et al.*<sup>220</sup> have extended the knowledge of the vitamin contents of dried meat to niacin, biotin, and folic acid. No significant loss of the

\* H.M. Stationery Office, 1/-.

former occurs under the most rigorous conditions, but folic acid behaves like thiamin.

In a series of papers Caldwell *et al.*<sup>221-223</sup> deal with the dehydration of many varieties of sweet peppers and the vitamin content of the products, Cruess<sup>224</sup> gives a useful general account of prune-drying in California and the question of blanching prunes *after* dehydration, in order to destroy enzymes, is discussed by Chari *et al.*<sup>225</sup> while Ulrich and Lafond<sup>226</sup>, who have studied storage conditions, recommend that prunes should be stored at 60% R.H.

The microbiology of 100 types of *frozen pre-cooked foods* has been found by Proctor and Phillips<sup>227</sup> to reflect the history of the food or food mixture. Pastry had the lowest population and creamed fish the highest. Pre-cooked foods should remain frozen until wanted for use.

Ulrich and Halvorson<sup>228</sup> have reported on the effect of rapid and slow freezing on bacteria and yeasts and state that slow freezing is the more detrimental to certain types, while quick freezing is the more detrimental to others; Gortner *et al.*<sup>229</sup> have investigated the effect of fluctuating storage temperatures on quality and conclude that it is the fact that storage temperatures have been above 0° for any considerable period, rather than the fact that they may have fluctuated, which does damage. Finnegan<sup>230</sup> suggests a practical method for determining the humidity of the air in a frozen food storage room—a matter of great importance with exposed foods or foods in non-moisture-proof packages. With a knowledge of the temperatures of the refrigerating coil and the air in the store, and the difference between them, the humidity of the air is obtained by reference to a chart compiled with the aid of a Bendix humidity recorder or an electric dew-point potentiometer.

The problems of cooking frozen foods by ultra-high frequency heating are described by Morse and Revercomb,<sup>231</sup> who find that foods tend to overheat at the points which thaw first; but the method was very rapid, a 12-oz. meal being heated from -15° to 23° in 70 seconds.

A novel method of freezing foods consisting of immersion in liquid nitrous oxide, which was in plentiful supply, was tried in Germany during the war and is described in B.I.O.S. Final Report 212 (also Food Manuf. 1947, 22, 263).

### *Sugar preserves and pectin*

Losses of ascorbic acid in preparing and storing fruit syrups and jams are given by Wendland,<sup>232</sup> who finds that ascorbic acid is more stable in jams than in syrups.

Pectin, its preparation and utilisation, are reviewed by van Oss<sup>233</sup> and Woodmaussee,<sup>234</sup> and pectin gels by Neukomm,<sup>235</sup> and these deserve study as the pectin industry has developed considerably on the Continent of Europe, especially in Germany and Holland. McCready *et al.*<sup>236</sup> describe the isolation and preparation of low-ester pectins and Deschreider and van den Driessche<sup>237</sup> review methods for estimating pectin in plant materials and recommend the method of Deuel, based on neutralisation and saponification with NaOH. This method is not applicable to jams, and precautions are necessary if reducing sugars are present. Fruit acids must be removed by precipitation.

*Acetic acid preserves* are well discussed by Burrell<sup>238</sup> and *loc. cit.* and *mayonnaise and related products* by Tritton.<sup>239</sup>

Among miscellaneous items are a plea by Pirie<sup>240</sup> for research on *leaf protein*, in view of world shortages; a description of the production of fodder-yeast containing 50–55% of protein from wood hydrolysates and still residues by is given by Harris *et al.*<sup>241</sup>; *detergency* in the food industries is discussed by Resuggan<sup>242</sup> in a series of papers, and the changes made in food regulations and laws in Australia since 1940 are detailed by Hinton.<sup>243</sup>

A review of the progress during 1947 in the analysis of most classes of foods is given by Grover,<sup>244</sup> and recent changes in the official and tentative methods of analysing many products, including foods, are published anonymously.<sup>245</sup>

### Vitamins and nutrition (general)

Much of the work on vitamins has been concerned with methods of assay, but Robinson<sup>246</sup> has given a concise, documented, and more general account, including discoveries in the therapeutic field, of work published in 1946. The reliability and possible sources of error in the chemical methods which are now available for estimating the various vitamins are discussed in two important papers by Harris, Mapson, *et al.*<sup>247,248</sup> and details of single methods are given by numerous authors, *e.g.*, the Carr-Price ( $\text{SbCl}_3$ ) method,<sup>249–251</sup> the spectrophotometric and chromatographic methods<sup>252–254</sup> and activated glycerol dichlorhydrin<sup>255</sup> methods for vitamin A. Lormand<sup>256</sup> has determined the vitamin A content of twelve marine fish commonly landed in Western France and hake is shown to be an important source. The extraction from hake livers is described.

For the vitamin B group the fluorometric determinations of thiamin, as thiochrome, is discussed by Roth,<sup>257</sup> Diemair and Fresenius,<sup>258</sup> and Bhagvat and Devi,<sup>259</sup> and its determination by adsorption and fluorometric methods by Daglish<sup>260</sup> and Williams and Wokes.<sup>261</sup> The extraction of vitamins  $B_2$  and  $B_1$  are discussed by Elvidge,<sup>262</sup> Rubin *et al.*<sup>263</sup> Watts *et al.*<sup>264</sup> and Ribeiro<sup>265</sup> (colorimetric, absorption, and fluorometric methods), the last-named giving the quantities of riboflavin found in a number of common vegetables grown in Brazil.

Rogers and Mickelson<sup>266</sup> have estimated the amounts of the various members of the vitamin B group, including folic acid, in different parts of the sugar beet and in its by-products. The highest folic acid content is in beet seed chaff, while beet molasses compare favourably with cane molasses in vitamin B content. The riboflavin production by 240 fungi grown on wheat bran has been studied by Peltier and Borchers.<sup>267</sup> Forty-five isolates gave values exceeding 2 mg. per 100 g. of mould bran, the highest yield being 5.8 mg. per 100 g. Synthesis of riboflavin is apparently common among soil moulds.

Chemical<sup>268</sup> and colorimetric<sup>269</sup> methods for determining nicotinic acid and the enzymic digestion of samples of food to liberate pantothenic acid for microbiological assay are described.<sup>270</sup>

A critical review of the 2:6-dichlorophenol-indophenol titration method for the determination of ascorbic acid is given by Souci<sup>271</sup> and

a micro-method is described by Gorbach.<sup>272</sup> Huelin and Stephens<sup>273</sup> describe how ferrous iron reduces 2:6-dichlorophenol-indophenol quantitatively in 3%  $\text{HPO}_3$  and may cause high results in the determination of ascorbic acid in canned foods. They suggest counteracting and precautionary measures. The relative merits of extracting ascorbic acid with  $\text{HCl}$  and  $\text{HPO}_3$ , from certain plant materials, are discussed by Sabalitschka and Marggraff.<sup>274</sup> Hartzler<sup>275</sup> finds that the colorimetric method gives false high values for the ascorbic acid content of stored guava juice and, in experiments carried out by Clayton *et al.*<sup>276</sup>; variations in canning procedure gave no significant variations in the vitamin C content of canned tomatoes. Sugar increases the stability of ascorbic acid in foods,<sup>277</sup> but such losses as are observed in sugar confections of various kinds are true losses and not mere changes into dehydroascorbic acid. They are generally related to the manufacturing process, and to factors such as storage time and temperature, water content, and  $p_{\text{H}}$ .<sup>278</sup>

Cheftel *et al.*<sup>279</sup> found ascorbic acid well preserved in conserve of rose hips and in the jelly from fresh and frozen blackcurrants provided that the jars were well filled, but some irreversible oxidation may occur in the surface layer.

Braun and Meyer<sup>280</sup> find ascorbic acid unstable in aqueous extracts of rose hips and set out the most favourable conditions for extraction. The ascorbic acid largely disappears after 17–24 hours. Comprehensive tables showing the ascorbic acid content of various fruit pulps, juices, and jams are given by Kuntz,<sup>281</sup> and Ezell *et al.*<sup>282</sup> have determined the ascorbic acid content of 28 varieties of strawberries. The range was from 38.9 to 88.9 mg. per 100 g. and berries grown in sunlight contained more than those grown in shade; also the increase during ripening is greatest when the fruit is allowed to ripen on the plants.

Two physico-chemical methods for determining vitamin D are compared by Ewing *et al.*<sup>283</sup> and a colour reaction<sup>284</sup> and a biological method<sup>285</sup> are described for determining vitamin K.

An account of the fortification of white wheat flour, margarine, etc., in the U.S.A. by addition of vitamins and salts during 1943–45 is given by Genevois and Dufrenoy.<sup>286</sup> In 1944, wheat flour was fortified with thiamin (4.4), riboflavin (2.7), and nicotinamide (35), Fe (29), and Ca (1100 mg. per kg.); margarine with vitamin A and D (20,000 i.u. per kg.), and dried milk with D (1600 i.u. per l. when reconstituted).

A brief account of the manufacture of food yeast is given by Thaysen,<sup>287</sup> and the working of a S. African plant using Thaysen's strain of yeast is described by Read.<sup>288</sup> A review of German work on this subject by Gemeinhardt<sup>289</sup> points out the important possibilities of yeast as an article of diet, and high figures for the nutritional value of two samples of *Torula utilis* and one of brewers' yeast are given by Goyco and Asenjo.<sup>290</sup>

Halden and Fleischanderl<sup>291</sup> discuss the biological value of soya products and give an outline of the development of the soya industry together with analytical data on soya beans and soya products and the losses which occur in processing. Diller<sup>292</sup> has an article on bread suitable for diabetics and Jesser<sup>293</sup> examines the effect of aluminium salts in baking powder on health. Gastric secretion is said to be unaffected by their use in normal amounts.

Van Schaik and van der Lee<sup>294</sup> have compared the times required for cooking vegetables and meat in pressure cookers and by normal methods, and have made observations on the taste, colour, smell, and nutritive values.

#### *Quality of foods (general)*

The value of organoleptic tests, *i.e.*, of observations by a trained tasting panel on the colour, flavour and appearance of foods in comparison with standards and in relation to chemical and physical tests, has been the subject of several papers.<sup>295-298</sup> Generally such tests are regarded as indispensable in judging quality, and one writer<sup>299</sup> asserts that subjective taste tests will detect changes of flavour, etc., several weeks before objective chemical tests.

Harding and Wadley<sup>300</sup> compare teen-age with adult palates for tasting oranges, and find the former more sensitive and critical.

Balavoine<sup>301</sup> discusses sensitivity in tasting various salts, including salts of toxic metals, and the masking of the taste of those by sugar, common salt, acid, etc., Fe is most easily detected, especially in inorganic combination, and toxic doses of most metals and of SO<sub>2</sub> and NH<sub>3</sub> can also be detected.

Tasting is stated to be the only satisfactory procedure for assessing the flavouring value of herbs,<sup>302</sup> and Daubert and Longnecker<sup>303</sup> state that bacon, smoked and treated with anti-oxidants, retains a good flavour five times as long as untreated bacon. The anti-oxidants tested were nordihydroguaiaretic acid, esters of gallic acid, thiodipropionic acid, and the tocopherols.

#### *Animal feeding stuffs*

A large number of papers on animal feeding stuffs have appeared, many of which seem to be either of purely local interest or merely confirmatory of, and capable of being deduced from, previous knowledge.

The conservation of grass by drying, ensilaging and haymaking is discussed by Woodman,<sup>304</sup> together with analyses of various products and certain feeding data for cattle, while Woodman and Evans<sup>305</sup> show that dried grass meal is palatable to pigs and can form about one-third of the ration for small pigs and one-fifth or one-quarter for pigs weighing more than 150 lb. Virtanen<sup>306</sup> has given a further description of his acid silage (A.I.V.) process. The  $p_H$  of this silage should not be below 3.0 (preferably, between 3.4 and 3.9) and the process entirely preserves carotene. Steensberg<sup>307</sup> and Heinzl<sup>308</sup> also refer to the A.I.V. process as causing the least waste, especially of protein and starch, but Steensberg places the  $p_H$  of good quality silage above 4.0. Both writers mention formic acid as a possible preservative for fodder, but it is said to be unsuitable for hard-stemmed plants.

The quantity of copper required in the diet of swine to prevent copper anaemia has been investigated by Carpenter,<sup>309</sup> who found that sows and gilts receiving 35  $\mu$ g. of copper per g. of diet had more numerous progeny than those receiving only 7  $\mu$ g. per g. Work on the effects of deficiencies of Mn, Cu, Co, and I, and on excesses of Se, Mo, and F in the diet are reviewed by Stewart.<sup>310</sup> Sunflower seed-meal<sup>311</sup> and also yeast<sup>312</sup> grown in sulphite-cellulose waste liquor have given good results in the diet of

fattening pigs, the yeast being slightly better than blood meal, while urea<sup>313</sup> and even ammonium bicarbonate<sup>314</sup> are mentioned as having been used successfully as substitutes for a proportion of the protein in the diet of cows.

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# THE FERMENTATION INDUSTRIES

By L. R. BISHOP, M.A., D.Sc., F.R.I.C. and T. J. WARD

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THE last two years have seen a rapid re-establishment of pre-war European conferences on subjects related to the fermentation industries and the release of much information acquired during the war. The following conferences have been held: the newly-formed European Brewery Convention at Scheveningen, Holland, in June 1947, The Fourth International Congress for Microbiology, Copenhagen, in July 1947, The International Congress of the Fermentation Industries, Ghent, October 1947, The Seventh International Congress of the Agricultural Industries, Paris, July 1948, and The Twenty-first Congress of Industrial Chemistry, Brussels, September 1948.

In Britain very important steps have been taken in furthering the Institute of Brewing Research Scheme by the appointment of Sir Ian Heilbron, D.Sc., LL.D., D.S.O., F.R.S., Professor of Organic Chemistry at the Imperial College of Science and Technology and President of the Chemical Society, as Director and in the purchase of a house and estate at Redhill for conversion into laboratories and an experimental station. The present position and future possibilities of the scheme have been described by R. Seligman<sup>1</sup> and discussed by B. M. Brown.<sup>2</sup>

The year has also been marked by the publication of a posthumous volume entitled "Barley," by the late Dr. E. S. Beaven; the first volume of a treatise in French, "Textbook of Brewing," by Professor J. de Clerck; a re-issue of "Biochemistry Applied to Malting and Brewing," by Professor R. H. Hopkins and the late B. Krause; a collection in book form of a number of papers published during the last ten years under the title of "Bottled Beer Quality," by the Wallerstein Laboratories; a new edition of A. Jørgensen's "Micro-organisms and Fermentation," rewritten by Albert Hansen and a Report on the German Brewing Industry, issued by H.M.S.O. (B.I.O.S. Final Report No. 1512)—this will be referred to subsequently under various headings.

The "Standard Methods of Analysis" of the Institute of Brewing have been revised and published with alterations and additions. Further details of these are given under the heading "Analysis."

## Barley

Earl (early-ripening Spratt-Archer) is stated to be the chief improvement in recent years in malting barleys.<sup>3</sup> H. Hunter<sup>4</sup> has discussed the influence of environment on yield and quality of some varieties with illustrations from the Irish Department of Agriculture experiments. The Scandinavian Maja and Kenia varieties are now being widely grown because of their early ripening and their short, resilient straw. The malts from these are not well liked for brewing, and the potentialities of

some Goldthorpe-Kenia crosses are indicated as well as that of winter-sown Pioneer.

Further results obtained in Sweden on mutant strains of barley produced by exposure to X-rays and likely to be of value in brewing are reported by H. Thunaeus.<sup>5</sup> Polish crosses to obtain a high-protein feeding barley gave a strain with over 3% nitrogen, but this was correlated with poor yield.<sup>6</sup>

A. C. Norman-Smith<sup>7</sup> has summarised the very considerable changes in the marketing of barley produced by shortages and by Governmental orders during and after the war. The rapidly increasing number of combine harvesters is mentioned and the objective of the Ministry of Agriculture is stated to be 10,000 by 1950.<sup>8</sup> The number of farm driers has by no means kept pace; neither, which is more disturbing, has it been possible to increase proportionately the drying facilities at maltings. An improved understanding has perhaps helped farmers to avoid major troubles in wet seasons, but the position each year becomes rapidly more dangerous. The characteristics of the barleys of the 1948 season are reviewed by H. L. Thompson.<sup>9a</sup>

In the circumstances rapid testing for damage to germinative capacity is very desirable and methods of using for this purpose 2 : 3 : 5-triphenyl tetrazolium chloride have been described by H. J. Cottrell,<sup>9</sup> by Messrs. May and Baker,<sup>10</sup> and by L. R. Bishop.<sup>11</sup>

That the damage to stored damp grain occurs through fungal growth is further demonstrated for wheat and maize by C. M. Christensen and D. R. Gordon,<sup>12</sup> who show that in the U.S.A. the species chiefly responsible are *Aspergillus glaucus*, *candidus*, and *ochraceous*, which can grow at low relative humidities. On inoculation they can cause heating of sterile damp grain, even (with a slightly longer delay) if only a small inoculum is used.

Mould damage can be prevented by suitable drying, and this is discussed by H. Hunter.<sup>13</sup> Storage in silos which can be ventilated with warm or cold air is described by E. P. Clarke and W. D. Vernon.<sup>14</sup> Local overheating may result from using infra-red radiation for drying so the writers are not in favour of the suggestion of M. Déribéré<sup>15</sup> that barley should be dried by this means.

Various phenylacetic acid derivatives (related to the plant growth hormones) were tested by R. Bawden<sup>16</sup> and found to have no beneficial effect on barley germination in dilute solution and stronger solutions (10<sup>-5</sup> g. per ml.) produced an initial retardation only.

## Hops

Reports have been published on the new varieties of hops grown in various countries: U.S.A.,<sup>17</sup> U.S.A. and Canada,<sup>18</sup> Belgium,<sup>19</sup> and Czechoslovakia.<sup>20</sup> The hop position in Germany is outlined in a B.I.O.S. Report.<sup>21</sup>

New varieties continue to be raised and tested at Wye by E. S. Salmon, who gives the 1946 results in his Thirtieth Report.<sup>22</sup> Two varieties resistant to downy mildew are Early Choice (Bramling type) and Concord (Golding

type).<sup>23</sup> They may act as carriers of mosaic disease but appear to be useful varieties. The new varieties have been shown in an exhibition<sup>24</sup> and discussed in a conference<sup>25</sup> and by J. Nott.<sup>26</sup>

The nutrient requirements of hops have been assessed by sampling and analysis of the plants at intervals through the season by J. Bonnet.<sup>27</sup> Progress in the study of hop cultivation at East Malling continues.<sup>28</sup> *Verticillium* wilt is one of the main studies<sup>28,29</sup> and some resistant varieties have been found.

The season's crop has been discussed by S. Myer.<sup>30</sup> A lime-sulphur-nicotine spray is stated<sup>31</sup> to be the most effective method of controlling red spider.

No benefit was found from the use of either  $\beta$ -indolylbutyric acid or  $\alpha$ -naphthaleneacetic acid in encouraging the rooting of hop cuttings.<sup>32</sup> The well-known benefit of cold storage in preserving the resin content was confirmed by laboratory experiments with Zatec hops.<sup>33</sup>

Large-scale brewing trials were made at two breweries on four varieties (OB 53, OM 26, 219, and OR 55) of hops showing resistance to *Verticillium* wilt, with a commercial variety as a control.<sup>34</sup> Numerous tasting trials showed that beers brewed with three of the varieties were preferred, but that from 219 was considered hard and inferior to the control.

Important progress has been made in the extraction and purification of the humulon and lupulon from hops, using first adsorption from a ligroin solution on a specially prepared silica gel,<sup>35</sup> followed by fractional elution with methanol and preparation of the pure  $\alpha$ -acid through the lead and *o*-phenylenediamine salts and the  $\beta$ -acid by crystallisation from ligroin at  $-15^{\circ}\text{C}$ .

Following this work a new method for the quantitative determination of the  $\alpha$ - and  $\beta$ -hop acids has been put forward by F. Govaert and M. Verzele.<sup>36</sup> The extracted acids are separated from impurities by chromatography on silica gel and the  $\alpha$ -acid estimated as the lead salt while the  $\beta$ -acid is estimated potentiometrically.

Further work has followed the transformation of humulon.<sup>37</sup> Heated in water it gives a mixture of two substances, but in methanol humulon was found to be quantitatively transformed into the isomeric isohumulon—an orange-yellow oil, which can be distilled *in vacuo*. After the extraction of large quantities of beer isohumulon was the only substance which could be identified. It therefore becomes of importance in discussing the real preservative effect of hops on beer.

The preservative effects of the original humulon and lupulon have been measured by the concentration just preventing growth and the findings of Shimwell and of Walker substantially confirmed by M. Hansens.<sup>38</sup> Yeasts are unaffected and so are Gram-negative bacteria; while, with Gram-positive bacteria, lupulon is inhibitory at a dilution of one in one to two million and humulon is effective in a concentration about twenty times greater. As was previously known, lupulon was shown to be much the less stable.

The organism used for the log-phase tests of antiseptic power by Walker and Hastings has been examined by D. Kulka and T. K. Walker<sup>39</sup> and found to be an active strain of *Lactobacillus plantarum*.

## Malting

H. A. D. Cherry-Downes<sup>40</sup> outlines the various methods of mechanising maltings in use on the Continent of Europe and America. He considers mechanisation to be increasingly urgent and the type chosen should be such as to give a continuous flow of material through the malting, so cutting down labour requirements evenly. Each malting must be considered individually to determine whether it is more economical to reconstruct or rebuild.

A. Topf drum installation in Sweden is described by R. K. Logan,<sup>41</sup> and the laboratory experimental malting plant at Nancy is described by E. Urien.<sup>42</sup>

The problem of modification through breakdown of the cell wall during malting is discussed afresh by I. A. Preece.<sup>43</sup>

## Biochemistry

### *Starch and the starch-hydrolysing enzymes*

A considerable number of papers have appeared dealing with starch, its components and the action on them of  $\alpha$ - and  $\beta$ -amylase. K. Myrbäck<sup>44</sup> has discussed the structure of starch, which is now established in general terms as consisting of helically coiled, straight-chain units of amylose containing 200–400 glucose units and one end-reducing group; while the other component is amylopectin consisting of branched chains of the amylose type connected by 1–6 instead of the usual 1–4  $\alpha$ -glucosidic linkages. Starches from different sources consist of different proportions of these two units. By the use of butanol, thymol, etc., the amylose can be crystallised out in a fairly pure condition, but the freedom of amylopectin from amylose is doubtful in many preparations and the enzyme results correspondingly inexact.<sup>45</sup> By a combination of the hot water separation and butanol or thymol crystallisation techniques K. G. Krishnaswamy and A. Sreenivasan<sup>46</sup> claim to have obtained both fractions pure.

The action of the two starch-hydrolysing enzymes on the two separate starch components has been studied on all four combinations<sup>47,48</sup> and  $\beta$ -amylase on amylopectin by J. E. Hodge, E. M. Montgomery and, G. E. Hilbert,<sup>49</sup> and on amylose by L. E. Harrison,<sup>50</sup> and by F. C. Cleveland and R. W. Kerr.<sup>51</sup> Briefly, the various workers agree that  $\beta$ -amylase forms maltose only and completely by repeated scission from the non-reducing end of the amylose chains. From amylopectin about 47% of maltose is formed and the residual complex dextrin left; whilst  $\alpha$ -amylase forms 6 to 7 glucose unit malto-dextrins from amylose, and malto-dextrins of 6 to 13 glucose units from the free branching chains of amylopectin, leaving the  $\alpha$ -amylor residual dextrin.

The conclusions from the enzymatic breakdown studies have received support from the investigations on the enzymatic synthesis of starch. The original (or P) enzyme of Hanes synthesises straight-chain amylose from glucose-1-phosphoric acid. The "Q" enzyme forms the 1–6  $\alpha$ -glucosidic linkages and produces the branched amylopectin either in conjunction with the "P" enzyme from glucose-1-phosphate or from amylose.<sup>52</sup>

The action of the amylases on unfractionated starch is that which would be expected from the behaviour of its components.  $\beta$ -amylase alone acting on starch produces 61% of maltose with some maltotriose from chains with an odd number of glucose units.<sup>53</sup> Similar findings using differential fermentations by different species of yeasts have shown disaccharides, trisaccharides, and dextrans in the products of the action of pancreatic amylase on potato starch.<sup>54</sup>

#### *Other carbohydrates*

By an elaborate system of fractionation K. Freudenberg, E. Plankenhorn and H. Knauber<sup>55</sup> have separated five different dextrans from the products of the action of *B. macerans* on starch and have confirmed that they are cyclic compounds.

By heating glucose or maltose with metaboric acid, dextrans containing 40–50 glucose molecules have been obtained.<sup>56</sup>

The preparation of maltose syrups from flour presents some difficulty and pre-extraction with cold water is necessary to remove part of the protein. Mould bran was an unsatisfactory source of enzyme but diastatic malt or amylase liquor from *Aspergillus niger* gave products which filtered satisfactorily and these could be refined by neutralisation with lime followed by clarification with charcoal and then bentonite.<sup>57</sup>

The presence of trisaccharides in wort has been shown by fractional fermentation by J. Blom and B. Schwarz,<sup>58</sup> and by V. I. Kudriavtzev.<sup>59</sup>

The polysaccharide of carrageen from the seaweed *Gigartina stellata* has been investigated by E. T. Dewar and E. G. V. Percival.<sup>60</sup> It yields 40% of galactose and contains 23.9% of the sulphate radical, but the formula cannot yet be decided.

Conditions for readily acetylating several sugars and polyhydric alcohols are given by S. D. Nicholas and F. Smith,<sup>61</sup> using acetic anhydride, acetic acid, and a small amount of perchloric acid in the cold.

Some methylated aldose sugars are oxidised with difficulty and cannot be determined by Fehling's solution, but these can be measured by oxidation with hypiodite, if the sugar solution and iodine are mixed and the alkali added drop by drop whilst the liquid is agitated.<sup>62</sup>

#### *Enzymes and vitamins*

A method for the determination of  $\beta$ -amylase activity has been published by G. Noelting and P. Bernfeld.<sup>63</sup> The maltose produced from amylopectin is determined from the brown colour formed with 3:5-dinitrosalicylic acid in alkaline solution. By a modification of Meyer's method contamination with 0.01% of  $\alpha$ -amylase may be detected.

S. Redfern<sup>64</sup> has introduced several modifications of the method of Sandstedt *et al.* for the estimation of  $\alpha$ -amylase, with the object of reducing the variability of results. I. A. Preece<sup>65</sup> has used a simple and effective method for the estimation of  $\alpha$ -amylase to study the conditions affecting its stability and the content in brewery malts. In kilning  $\alpha$ -amylase is inactivated much less rapidly than  $\beta$ -amylase, but  $\alpha$ -amylase may decrease during storage. The relation between the  $\alpha$ -amylase

activity and D.P. of malt is fair, but too approximate for any deductions to be drawn.

A. D. Dickson, W. J. Olsen, and H. L. Shands<sup>66</sup> have studied the effect of flooring conditions on the  $\alpha$ - and  $\beta$ -amylase activity of malts. Flooring temperatures above 61° F. led to a more rapid development, but no final increase in the  $\alpha$ -amylase activity. Neither was this affected by the moisture content during flooring. On the other hand, higher moisture contents usually led to the production of higher  $\beta$ -amylase activity and the speed of its production increased with temperatures above 54° F. Variety of barley and soil and seasonal conditions were all found to effect the  $\alpha$ - and  $\beta$ -amylase activities of the malts.<sup>67</sup>

T. M. Back, W. H. Stark, and R. E. Scalf<sup>68</sup> have elaborated a method of testing for "limit dextrinase" activity on a standard limit dextrin. The activity is stated to be little affected by  $\alpha$ - and  $\beta$ -amylases and to be higher in preparations from *Aspergillus oryzae* and Mylase bran than in those from barley malt.

An explanation of their results may be provided by the results of J. Corman and A. F. Longlykke,<sup>69</sup> who find that the alcohol yields from corn mashies agree most closely with the glucose-forming activity of different mould enzyme preparations.

Several workers have made progress with the purification of the amylases. S. Schwimmer<sup>70</sup> used fractional adsorption on bentonite of an autolysed malt extract and elution with 5% pyridine followed by fractional precipitation with ammonium sulphate. H. Lundin<sup>71</sup> used repeated fractional precipitation with ammonium sulphate and dialysis. Both  $\alpha$ - and  $\beta$ -amylase activities were found to be associated with the albumin fraction (as shown by Osborne) and the two could not be separated from one another by electrophoresis. C. E. Danielsson<sup>72</sup> has determined the molecular weight of such a preparation from ultra-centrifugal and diffusion measurements and found a value of 54,000.

Malt  $\alpha$ -amylase has been purified and crystallised by S. Schwimmer and A. K. Balls.<sup>73</sup>

Purification of *Aspergillus oryzae* amylase has been studied by R. L. Gates and E. Kneen.<sup>74</sup>

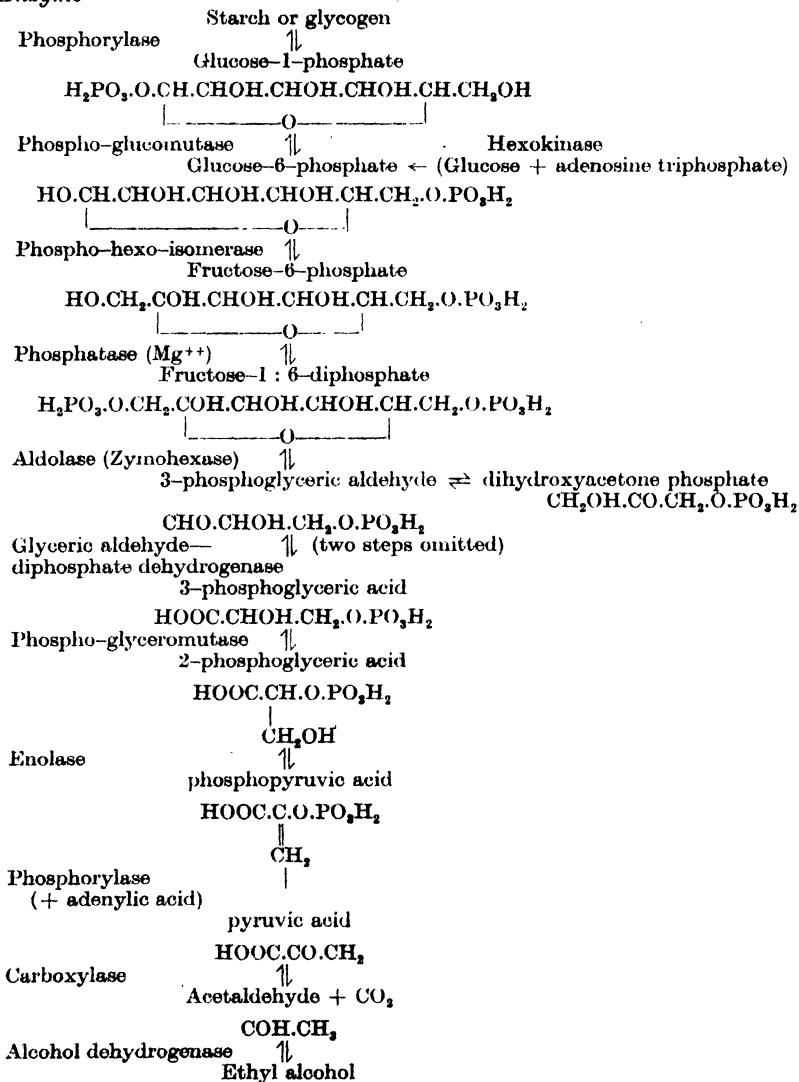
The relationship between cytase activity and modification is discussed by I. A. Preece.<sup>75</sup>

The oxidising enzymes of barley and malt have been the subject of several studies: *o*-phenylenediamine oxidase,<sup>76</sup> peroxidase,<sup>77</sup> and pyrogallol-oxidase<sup>78</sup> and peroxidase in malt adjuncts.<sup>79</sup>

The very important progress made in enzyme chemistry in recent years has been summarised by J. A. V. Butler in a series of lectures which have been reprinted.<sup>80</sup> Enzymes are now isolated as crystalline proteins and their homogeneity tested by ultra-centrifugal, diffusion, and solubility techniques. Further stages now becoming customary are the identification of the prosthetic groups (either vitamins or trace metals) and the integration of the enzyme function into the metabolic sequence in the living cell. As a result a complete understanding of the fermentation-muscle glycolysis sequence and the respiration sequence is being approached.

The fermentation sequence is fundamental to the subject-matter of this review and Butler's summary is reprinted here.

### Enzyme



The following matters of interest in connection with this fermentation sequence have arisen recently. A paper on the kinetics of cell-free fermentation by O. Meyerhof.<sup>81</sup> Yeast hexokinase has been purified and crystallised by K. Bailey and E. C. Webb.<sup>82</sup> Its activity is inhibited by poisons for the -SH group. Aldolase has been crystallised by J. F.

Taylor, A. A. Green, and G. T. Cori.<sup>83</sup> D-glyceraldehyde-3-phosphate dehydrogenase has been crystallised by G. T. Cori, M. W. Slein, and C. F. Cori,<sup>84</sup> and its prosthetic group has been shown to be diphosphopyridine nucleotide.<sup>85</sup>

Recent activity has centred particularly on identifying the enzymic functions of the vitamins. Pantothenic acid appears to function as co-enzyme A in acetylation,<sup>86</sup> but O. E. McElroy and A. Dorfman<sup>87</sup> consider that the pantothenic-containing enzyme is concerned with the utilisation of acetyl methyl carbinol or some closely-related substance.

Pyridoxal and pyridoxamine are essential for the conversion of indole and anthranilic acid to tryptophan by *Lactobacillus arabinosus*.<sup>88</sup> The principal bound form in which B<sub>6</sub> occurs appears to be pyridoxamine phosphate.<sup>89</sup> It or pyridoxal phosphate functions as the glutamic-aspartic trans-aminase.<sup>90</sup> The aspartic-alanine trans-aminase appears not to be a separate enzyme but the product of glutamic-aspartic and glutamic-alanine trans-aminases.<sup>91</sup> Pyridoxamine phosphate functions as a growth factor for *Lactobacillus helveticus*.<sup>92</sup>

Pteric acid and pteric-glutamic acid conjugates (folic acid) appear to function in the biosynthesis of purines and thymine.<sup>93</sup> W. H. Prusoff, L. J. Teply, and C. G. King<sup>94</sup> obtained evidence that P.G.A. functions in the synthesis of deoxyribonucleic acid but not of ribonucleic acid. *p*-Amino benzoic acid provides part of the P.G.A. molecule, and this may entirely explain why it has been found to function as a vitamin, but there are suggestions that it may also have independent functions.<sup>95</sup>

Biotin appears to be related to oxalacetic decarboxylation,<sup>96-99</sup> and may play a rôle in the synthesis of oleic acid.<sup>100</sup> It is doubtful if it functions in aspartic acid decarboxylation.<sup>101</sup>

Putrescine appears to be a growth factor for *Hemophilus parainfluenzae*.<sup>102</sup>

It will be noted that a number of the vitamins, including streptogenin, appear to be of a simple peptide nature. On the other hand, several peptides function as antibiotics (*e.g.*, gramicidin), and lycomarasmin (which causes wilt in tomatoes) is believed to be a simple peptide containing asparagin and  $\beta$ -hydroxyalanine.<sup>103</sup>

#### *Vitamins in cereals and brewing materials*

The recent studies by numerous authors on the effect of germination on the vitamin content of cereals are reviewed by F. W. Norris.<sup>104</sup> During the germination of barley, biotin, pantothenic acid, and pyridoxine increase significantly and riboflavin increases 60-80%. On the other hand, there is a slight loss of aneurin, and nicotinic acid is unchanged in amount. A further summary gives the results of numerous investigators working on the amounts of aneurin, riboflavin, nicotinic acid, pyridoxin, pantothenic acid, and biotin in barley, malt, wort, yeast, and beer.<sup>105</sup> These summaries should be consulted for further references.

The distribution of aneurin in the grains of barley, wheat, oats, and rye has been studied by L. H. Pulkki and K. Puutula.<sup>106</sup> They have confirmed that in barley, wheat, and rye the vitamin is in or near the germ, but in oats it is more evenly distributed.

E. M. James, F. W. Norris, and F. Wokes<sup>107</sup> found good agreement between the results obtained by a chemical and a micro-biological method in the determination of nicotinic acid in barley and yeast.

The pyridoxin content of Belgian beers has been reported by M. Van Laer and R. Storek,<sup>108</sup> and of British beers by R. H. Hopkins and R. J. Pennington.<sup>109</sup>

Pantothenic acid in brewing has been studied by R. H. Hopkins, S. Wiener, and C. Rainbow.<sup>110</sup> Some types of brewing yeast increase the vitamin content of the beer whilst others decrease it or have no effect.

Out of a number of single-cell cultures of English brewery top-fermentation yeasts, two strains were found which required *p*-aminobenzoic acid in addition to the usual yeast-growth factors.<sup>111</sup>

Two hundred and forty species of moulds were grown on yeast bran and tested for riboflavin production. The greatest yield was given by a "gold" *Aspergillus* followed by some *Fusarium* species.<sup>112</sup>

### Disinfectants, sterilisation, and the preservation of beer

Studies in this field have been active. Newer types of disinfectants are being developed, and both with these and the older types the mode of action is being investigated with a view to their more effective use.

The high antiseptic value of chlorine is well known. Although this is effective in concentrations of the order of 0.1 p.p.m. (where the "chlorine demand" is low) from studies by H. C. Marks, O. Wyss, and F. B. Strandkov,<sup>113</sup> it would appear that the chief antiseptic action is due to hypochlorous acid formed by hydrolysis. Of this only the undissociated molecule is effective so that the action is maximal at  $p_H$  6.

In this and all other actions where only trace amounts are needed there is a high probability that the effect is due to interaction with an enzyme system. With chlorine it has been shown that the killing time is closely related to the action on glucose-oxidising enzymes,<sup>114</sup> and triosephosphate dehydrogenase appears to be the most susceptible.

Bromine and iodine are of the same order of potency but here only part of the activity appears to be due to the corresponding hypo acids.<sup>115,116</sup> With iodine an interesting claim of A. J. Salle<sup>117</sup> is that the antiseptic activity is increased many times by the presence of a 1 in 3000 dilution of an oxidation-reduction system, such as manganous and ferric sulphates.

With iodine the specific function causing the antiseptic action appears to be inhibition of zymoheaxase, presumably by the oxidation of sulphhydryl groups.<sup>118</sup>

Sulphur dioxide is only effective in the "free" state and studies of its action on yeasts in nutrient solutions containing glucose at two different concentrations show that the "free"  $SO_2$  can be measured by iodine titration. However, in fruit juices there appear to be factors which reduce the effectiveness of the iodine-titratable  $SO_2$ .<sup>119</sup>

A number of the new antiseptics are being developed following the work and theories of Wood, Fildes, and McIlvain, aimed at specific enzyme systems by blocking with a non-functional analogue of the vitamin constituting the prosthetic group of the enzyme. The development, for instance of phenylpantothenone as an antagonist of pantothenic acid is an example, and the subject of the anti-vitamins has been reviewed

by C. Heymans.<sup>120</sup> Since the success of the sulphonamides this line does not appear to have led to much practical success and other paths are being actively followed.

In a number of enzyme systems the active group is one of the metals necessary for growth in trace amounts. Combination with the trace metal explains the activity of many older toxic or antiseptic substances such as sodium azide. This combination also explains the antiseptic action of the so-called chelating agents—organic compounds to which a metal is firmly bound both by replacing the hydrogen of an hydroxyl group and by a “co-ordinate” bond with an adjacent nitrogen atom. If the compound is able to penetrate living cells the resultant insoluble precipitate removes the active metal and effects antiseptis. The well-known antiseptic action of 8-hydroxyquinoline is explained in this way (see discussion and references by W. O. Kermack<sup>121</sup>), and so are the earlier observations of T. K. Walker, H. H. H. Hastings and E. Vero,<sup>122</sup> where concentrations of this compound were found to have no effect below a critical value and thereafter to have an action proportional to the concentration. A. Albert, S. D. Rubbo, R. J. Goldacre, and B. G. Balfour<sup>123</sup> have shown that with Gram-positive bacteria and Gram-negative cocci the inhibition is reversed by the addition of cobalt, which therefore is presumably the trace metal involved. With Gram-negative bacteria, iron, zinc, or copper appear to be variously involved.

On the other hand, the antiseptic effect of phenol and the newer quaternary ammonium disinfectants the action appears to be related to their denaturing effect on proteins and through this and the action on lecithin to the breakdown of the semi-permeable membrane of the cell wall, since the loss of cell solutes to the medium is proportional to the bacteriostatic effects, as was shown by Hotchkiss<sup>124</sup> and confirmed by Gale and Taylor.<sup>125</sup> The actual breakdown of the bacterial cell wall has been shown in electron-photos by Mitchell and Crowe.<sup>126</sup>

Because of the low concentrations required and of the chemical stability and the absence of taste and smell and adverse effects on the skin there have been proposals to use quaternary ammonium compounds in sterilising brewery plant from the mash-tun to the fermenting vessels by G. J. Lehn and R. L. Vignolo<sup>127</sup> and J. Christoffersen<sup>128</sup>; and their use for sterilising glasses in public houses has been further advocated by J. G. Davis and J. C. L. Resuggan.<sup>129</sup>

Since many different groups may be used as substituents in each of the hydrogen atoms of these ammonium compounds, more than a 100,000 possibilities exist, and the discovery of the most effective is bound to take a long time. One of the requirements for effectiveness appears to be that at least one of the four radicals shall be a long carbon chain.<sup>130</sup> When the nitrogen atom forms part of a cyclic nitrogenous substance, only one radical remains to be substituted and here the cetyl radical appears effective as in cetyl pyrimidium chloride (“Ceepryn”). Most “quats” lose their efficiency in acid solution but the compound named appears to be as effective at  $p_H$  3 as at 8.<sup>131,132</sup>

The quaternaries are surface-active, which explains at least part of their antiseptic action and why they act also as detergents. In addition the surface activity makes results by the usual tests—such as the phenol

coefficient—misleading, and a considerable discussion still ranges round the best way of testing their efficacy.<sup>133,134,135</sup>

In spite of the doubt about their exact antiseptic values it is fairly safe to conclude that, although some are very high, they are less effective bacteriologically, particularly against Gram-negative bacteria, than hot water, steam, or hypochlorites, but against this must be put their convenience and the absence of undesirable effects.<sup>136,137</sup>

Various methods have been proposed for the estimation of quaternaries, many of which rely on combination with a dye such as bromphenol blue.<sup>138,139,140,141</sup> Comparative tests have been made of twenty-one methods.<sup>141a</sup>

Attempts have been made in some countries to utilize certain types of trace inhibitors for a form of "cold sterilisation" of beer, and esters of monobromoacetic acid are mentioned by A. Hansen in "Micro-Organisms and Fermentation," p. 132

## Yeasts

A simple summary of the morphology of yeast has been given,<sup>142</sup> and ascospore formation is dealt with by H. J. Phaff and E. M. Mrak.<sup>143</sup> The classification of yeasts by morphological characters presents considerable difficulty and an agreed conclusion is by no means reached. The subject is too extensive for consideration here and is fully reviewed in the 1948 "Annual Review of Microbiology."<sup>144</sup> In industrial use the morphological characters are of importance in identification, but the primary interest is in the products of the metabolic activity and studies of the biochemical characteristics are being developed. O. Winge and C. Roberts<sup>145</sup> have studied the transmission of enzymic characters by hybridisation. E. Paynaud and J. Ribereau-Gayon<sup>146</sup> have studied the by-products produced by 29 strains of elliptic yeasts. The sum of the various by-products was very constant, but there were large variations in the proportions of these. The ratios of butyleneglycol to glycerol and of acetic to succinic acid were used as the basis for distinguishing six physiological types. Another means of biochemical sub-classification is that suggested by A. S. Schultz, L. Atkin, and C. N. Frey<sup>147</sup> on the basis of the vitamin (or bios) requirements of the strains. This idea has been worked out by A. S. Schultz and L. Atkin<sup>148</sup> and strains of *Saccharomyces* have been given a "bios number" according as the yeast is deficient in one or more of seven vitamins, and the addition of letters to denote the sugars fermented has been suggested. The vitamin requirements of two yeast strains produced from a brewery yeast by acenaphthene, one of which is stated to be a tetraploid, are recorded by M. P. Bai.<sup>149</sup> Related studies by K. K. Mitra<sup>150</sup> claim higher growth and attenuating rates for an acenaphthene tetraploid yeast. A. Skovsted<sup>151</sup> has confirmed the production of mutants from yeast by the action of camphor, but considers that there is no evidence that it produces polyploidy.

Basic dyes containing a quaternary nitrogen atom, such as methylene blue, crystal violet, and methyl green, when used at a low concentration (below  $10^{-4}$ ) inhibit multiplication of yeast cells without inhibiting respiration, but higher concentrations inhibit respiration. This action is shown by L. Massart and G. Peeters<sup>152</sup> to be due to combination with

the nucleic acids. The dyes can be displaced by metals, the trivalent ions being much the most effective and the divalent next in effectiveness. The dyes can also be withdrawn by nucleotides in the medium and the inhibition of respiration removed.

The site of the alkaline phosphatase in yeast has been studied by W. J. Nickerson, E. J. Krugelis, and N. Andresen<sup>153</sup> by the Gomori cobalt sulphide staining technique. The site indicated varied with the substrate. By using pyrophosphate an association with desoxyribose nucleic acid in the nucleus was indicated. With hexametaphosphate, general staining occurred and association with ribose nucleic acid was indicated.

The fundamental importance of phosphoric acid in cell reactions is now well known and the forms in which phosphorus exists in yeast are discussed by J. M. Wiame.<sup>154</sup> Orthophosphate, nucleic acids, acid-soluble and acid-insoluble metaphosphate have been estimated and the proportions shown to vary widely with the state of phosphorus nutrition of the yeast.

S. Hestrin<sup>155</sup> contributes a review of the evidence that disaccharides are fermented directly instead of previously undergoing hydrolysis to monosaccharides, as in the original Fischer postulate. The evidence for direct fermentation appears strong, but it is noteworthy that, in the studies quoted, and indeed on most studies of the fermentability of sugars the technique has usually been to add yeast to a pure or fairly pure solution of the sugar. In these circumstances, it is considered likely by the reviewers that the rate of fermentation observed is dependent on the limited supply of nutrients, rather than the nature of the sugar. For instance, preparations of maltose are commonly more contaminated with nutrients than glucose and faster fermentation is therefore likely to occur in solutions of the former sugar. Similar considerations apply to studies of the assimilation of nitrogen compounds, for instance, Lodder<sup>156</sup> used "auxinographic" studies to investigate the assimilation of nitrogen compounds. In this method the compound to be tested is placed as a spot on an agar-synthetic medium in a Petri dish containing an even suspension of the yeast. If the compound is nutritive then growth of the yeast occurs round the spot. Using this technique, Lodder concluded that certain yeasts could only utilise peptone as a nitrogen source. H. Brown<sup>157</sup> had previously come to the same erroneous conclusion. Later work by Wickerham<sup>158</sup> showed that the peptone (which in the pure state is almost certainly non-assimilable) had served as a source of nutrients lacking from the medium. The opinion advanced here is that all tests of this type should be made by one or both of two techniques. One technique must ensure that the medium contains a sufficient supply of all nutrients, as shown by the attainment of "full wort growth" as defined by L. R. Bishop and C. Rainbow<sup>159</sup>; that is growth in the synthetic medium should equal the best growth observed in a natural or supplemented natural medium, indicating that no extraneous limiting factor was intervening. The other technique, which can be employed if the nutrient liquid is not a complete source of bios, is to employ nitrogen compounds or sugars produced synthetically to measure assimilability or fermentability: thus ensuring that the compound added does not

at the same time convey bios, which is very frequently present in compounds isolated from natural sources.

Some interesting experiments on the effects of progressive washing of yeast have been recorded by E. S. Taylor.<sup>160</sup> Yeast in the absence of glucose accumulates glutamic acid from the medium in its cells, on the addition of glucose this glutamic acid is further metabolised. Such depleted cells can synthesise glutamic acid in the presence of glucose and ammonia. Pre-washing the yeast destroys the ability to synthesise glutamic acid but this may be restored by addition of the bios complex. After moderate washing pantothenic acid alone restores the function. After more thorough washing biotin and pantothenic acid are necessary. After exhaustive washing the other members of the bios complex are also needed. These findings can be related to the specific functions discussed under enzymes: full biotin supply being required for assimilation of ammonia and full pantothenic acid supply for the synthesis of glutamic acid.

Pitching yeasts treated for 12 hours with 5000 I.U. of penicillin were unharmed and were freed from acetic and lactic bacteria.<sup>161</sup>

Yeasts grown in media containing acetic acid are known to accumulate fat, by studies with isotopically labelled carbon A. C. G. White and C. H. Werkman<sup>162</sup> showed that acetate is directly converted to fat and that the synthesis is not *via* carbon dioxide.

If a capsule-forming yeast, such as *Torulopsis rotundata*, is grown in a synthetic medium containing mineral salts, aneurin and glucose, a polysaccharide can be precipitated from the liquid by alcohol. The polysaccharide gives a blue colour with iodine and yields glucose and xylose on hydrolysis. Freezing precipitates an amylose-like substance and leaves pentose-like material in solution. The yeast and its press-juice can produce starch from glucose-1-phosphoric acid, indicating the presence of a starch-forming enzyme.<sup>163</sup>

G. Wilharm and U. Sack<sup>164</sup> tested 20 yeast strains for ability to produce ethyl alcohol from lactose. The most effective utilised 95% of the lactose in whey. The optimum conditions were 30° C., lactose concentration 6.5–7.5% with continuous agitation.

Methods for determining the quantity of yeast suspended in a liquid have been surveyed by J. White.<sup>165</sup> The "gravity column" method has been applied to measure the specific gravity of yeast suspensions by L. Atkin.<sup>166</sup>

The beer-spoilage organisms contaminating brewery pitching yeast are stated by J. J. Olshausen<sup>167</sup> to be mostly Gram-positive and catalase-negative and therefore these two tests are of considerable value in the examination of pitching yeast. This viewpoint should be compared with that of Shimwell reported under Micro-biology.

E. Helm<sup>168</sup> argues the advantages of using pure culture yeasts in brewing and describes the technique for obtaining a pure yeast culture for pitching. A. C. Thaysen<sup>169</sup> describes the micro-manipulator, which can be used for cell or spore isolation.

M. Gocar<sup>170</sup> has summarised the very varied ways in which yeast is of value to humanity.

J. A. Goyco and C. F. Asenjo<sup>171</sup> have compared the food value of nutrient yeast (*Torulopsis utilis*) with brewers' yeast and have found

that, in spite of a slightly lower digestibility, the latter had a higher biological value and net protein value.

The method of large-scale manufacture of *T. utilis* from cane molasses has been described by H. J. Bunker.<sup>172</sup> A description of a similar pilot plant in South Africa is given by F. O. Read.<sup>173</sup> Conditions for producing the same yeast from waste bisulphite liquors are described by C. Arnaudi, J. Politi, and C. Cella,<sup>174</sup> and the German Waldhof process is described by J. M. Holderby.<sup>175</sup> The adaptation of *T. utilis* to wood hydrolysates is described by E. E. Harris *et al.*<sup>176</sup>

### Microbiology

A general survey of bacteriology from the brewing standpoint by J. L. Shimwell is being serialised in the Wallerstein Laboratory Communications.<sup>177</sup> Relation to environment, sterilisation, and disinfection, classification, and identification, acetic acid bacteria and Gram-negative bacteria in wort, yeast, and beer are dealt with.

The nomenclature of the brewery lactic acid bacteria has been revised and classified by J. L. Shimwell.<sup>178</sup> Their nutritional requirements are complex: they are reviewed by E. E. Snell.<sup>179</sup>

New strains of *Acetobacter suboxydans* have been isolated from pitching yeast and beer and described by D. Kulka and T. K. Walker.<sup>180</sup> These authors<sup>181</sup> have also disputed Shimwell's contention that capsules of *A. turbidans* cannot be demonstrated by the flagella stain of Plimmer and Paine.

E. G. Bousfield, G. G. H. Wright, and T. K. Walker<sup>182</sup> have shown that some species of *Acetobacter* are able to oxidise glycerol to dihydroxyacetone in yeast-water medium. Other species failed to produce dihydroxyacetone and others again failed to grow in the medium. These differences may be of value in the diagnosis of species.

One form of ropiness in beer is due to *Acetobacter viscosum* or *capsulatum*.<sup>183</sup> Air is necessary and dextrin assists the formation of rope, which appears to be of carbohydrate character. Hop resin and  $p_H$  adjustment have no effects. A later paper<sup>184</sup> describes another form of ropiness due to two varieties of *Streptococcus damnosus*—*viscosus* and *limosus*. The latter is a vigorous rope producer, but the conditions favouring its production are the opposite of those for *Acetobacter* rope. *Streptococcus* rope is favoured by anaerobic conditions, sugars, low hop rate and high  $p_H$ .

M. Lemoigne<sup>185</sup> has shown that the reserve fatty material found in members of the genus *Bacillus* consists almost exclusively of polymerised  $\beta$ -hydroxybutyric acid.

B. P. Cardon and H. A. Barker<sup>186</sup> have isolated two species of bacteria fermenting amino acids. *Diplococcus glycinophilus* utilises only glycine with the production, anaerobically, of acetate, carbon dioxide and ammonia. These authors, with B. E. Volcani<sup>187</sup> have shown, by using C<sup>14</sup> labelled glycine, indications that the main reaction is a condensation of two molecules of glycine by their methylene groups followed by liberation of CO<sub>2</sub> from the terminal carbon atoms and oxidation of the two central carbon atoms to acetic acid. *Clostridium propionicum* can utilise a number of amino acids with the production of propionate, and other

acid radicles, such as acetate, together with carbon dioxide and ammonia.

A. J. Kluyver and C. G. I. P. Schnellen<sup>188</sup> have shown that *Methanobacterium omelianskii* can utilise carbon dioxide and hydrogen to produce methane and water, while *M. barkeri* can carry out this reaction after having, in addition, produced carbon dioxide and hydrogen from carbon monoxide and water.

### Methods of analysis

An event of importance to all brewers' and maltsters' chemists is the publication by the Institute of Brewing<sup>189</sup> of revised methods for the industrial analysis of malts. These came into operation on 1st September, 1948, and are based partly upon improvements in procedure which have developed since the previous revision in 1933. Minor modifications have been made in the methods for determination of moisture and diastatic power, and procedures for the determination of total nitrogen in malt and barley and permanently soluble nitrogen in wort have been added. The chief modification is in the calculation of the extract which now eliminates the error due to the assumption that the volume occupied by the grains is 15 ml. The new calculation is derived from recent work, both practical and theoretical, by Bishop, Cuff, and Hickson, and yields results approximately 1 lb. higher than those obtained by the previous method for malts in the normal extract range.<sup>190,191</sup> The subject is also discussed by L. R. Bishop.<sup>192</sup> The alteration involves slight revision of the constants in the equations for prediction of extract.<sup>192a</sup>

Further discussions on the methods of malt analysis have been published by H. E. Kelly and T. S. Bremner.<sup>193</sup> Their observations include the interesting point that a number of malt mills may be set to the 0.5 mm. gauge, but, when the same malt is ground in them a sieving test shows distinct differences in the proportions of material of different sizes in the grists, which appear to affect the extract results considerably. In this connection, it is interesting to note the American test mentioned by A. J. C. Cosbie,<sup>194</sup> in which soft metal wire is run through the mill and the thickness measured. This may prove a better test than the feeler-gauge alone.

The methods of analysis standardised in France are reported by E. Urion<sup>195</sup> and given in a book.<sup>196</sup>

B. H. Nissen<sup>197</sup> has reported photo-electric measurements of beer colour using green, blue, and white colour filters.

Methods for the determination of air and oxygen in beer and wort have been the subject of papers by M. Roberts, S. Laufer, and E. D. Stewart.<sup>198</sup> In commercial brews the worts were found to contain per litre 12–15 ml. of air and 3 ml. of oxygen. These were reduced to minimal amounts during fermentation, but increased later to about 4 ml. of air with 0.3 ml. of oxygen. Further results showed that most of this air and oxygen are introduced during bottling.

A manometric method for the determination of carbon dioxide is described by I. Stone.<sup>199</sup>

A method which may be adapted to the determination of sulphur dioxide in beer involved the formation of a red colour in a reagent produced by the reduction of fuchsin with formaldehyde.<sup>200</sup>

A survey of all the many procedures proposed as modifications of the Kjeldahl nitrogen determination has been made by A. Hiller, J. Plazin, and D. D. van Slyke.<sup>201</sup> As a result of the survey and of further tests they conclude that digestion in the presence of mercury and distillation with powdered zinc gives the most accurate results.

The determination of arsenic in brewing materials is the subject of a survey article by "Linkman."<sup>202</sup> For the determination of zinc in beer, titration with dithizone is considered to be satisfactory.<sup>203</sup>

The recent modifications in the method of determination of alcohol in potable spirits prescribed by the American Bureau of Customs are described by J. F. Williams and E. F. Kenney.<sup>204</sup> The new modifications include addition of salt before distillation with samples containing 50-70% of alcohol and the use of correction tables for weighings at temperatures above 15.56° C. M. Besson<sup>205</sup> finds that water in dehydrated methanol and ethanol can be determined by the Karl Fischer reagent, but the accuracy is reduced if aldehyde and ketones are present.

Glycerol in fermentation residues can be determined by first precipitating them with lime and alcohol. After concentration of the filtrate, distillation with periodic acid converts the glycerol to formaldehyde, which is distilled off and determined by adding  $\text{Na}_2\text{SO}_3$  and titrating with standard acid. Alternatively, a polarographic method is used.<sup>206</sup>

The determination of glutathione in yeast has been made more reliable by T. Astrup and V. Øhlenschläger,<sup>207</sup> who have shown that pre-treatment with trichloroacetic acid gives a full yield, but that if metaphosphoric or salicylsulphonic acid is used instead then only partial recovery is obtained.

The colorimetric method for starch determination devised 12 years ago by G. W. Pucher, C. S. Leavenworth, and H. B. Vickery has been modified.<sup>208</sup> The starch is extracted with perchloric acid and precipitated with iodine. After regeneration of the starch and its hydrolysis with acid, the sugar is determined colorimetrically by Somogyi's phosphate reagent with potassium iodate added.

The conditions for the accurate determination of sugars in the presence of non-sugar compounds has been studied by J. Blom and C. O. Rosted.<sup>209</sup> The most correct results are obtained with reagents containing copper since these have the lowest oxidation-reduction potential. The use of tartrate in Fehling's solution makes the reagent unstable through slight auto-reduction. The authors decide in favour of a reagent containing copper sulphate, potassium carbonate, and bicarbonate. After heating with the solution under test, either potassium iodide is added and the liberated iodine is titrated with 0.1-N sodium thiosulphate, or the Lane and Eynon method is used.

Nitrites introduce considerable errors in the iodometric determination of sugars, but the addition of urea to the hot acidified solution eliminates the error.<sup>210</sup>

Sodium starch glycoolate can be readily prepared as a white powder. It is soluble in water to form a stable solution which serves as a good indicator for iodimetric analysis.<sup>211</sup>

Glucose can be determined colorimetrically (at 6500 Å.) by measurement of the blue colour formed by the reduction of molybdates.<sup>212</sup> The

method is satisfactory in the presence of moderate amounts of sucrose and other di- and trisaccharides.

A chromatographic method for the separation of methylated sugars is described by F. Brown and J. K. N. Jones.<sup>213</sup> The paper strip chromatography of sugars is described by S. M. Partridge.<sup>214</sup> A symposium on partition chromatographic methods has been held by the Biochemical Society.<sup>215</sup>

A similar symposium has been held on "Quantitative Biochemical Analysis by Micro-biological Response."<sup>216</sup> Micro-biological methods appear to be satisfactory when applied to the hydrolysates of pure proteins but less so when used for complex biological extracts.

## Beer and the brewing process

### *Technical*

Several accounts have appeared of the Danish breweries and brewing industry.<sup>217, 218, 219</sup>

The weak beers brewed in Germany are described by G. Goy<sup>220</sup> and in a B.I.O.S. report.<sup>21</sup> The abnormal tastes of weak beers—the chlorine-like odour due to reduction of nitrates and the phenolic odour due to bacterial decomposition of tyrosine—are described by Y. Deux.<sup>221</sup> Both are cured by adjustment of the beer to  $p_H$  4.0.

The same author<sup>222</sup> describes how molasses can be treated to give an acceptable flavour to beer. Other abnormalities of beer flavour and their eradication are considered by D. G. Ruff.<sup>223</sup>

An ultra-violet lamp emitting at about 2650 Å. is used in America for the destruction of infecting organisms in bottles, etc.<sup>224</sup> General recommendations for the improvement of beer stability are given by A. Schmal.<sup>225</sup> A process for increasing the stability of beer has been patented by A. H. Hughes and A. Guinness, Son and Co. Ltd.<sup>226</sup> In this process 0.02 to 0.2% of egg white is added to beer prior to racking.

E. Rausch<sup>227</sup> claims that modern improvements have made steam boiling yield more satisfactory results than fire boiling, by reducing the risk of caramelisation of the worts. A. Slator and J. H. St. Johnston<sup>228</sup> have made comparison brews with worts boiled in the ordinary way with a gas-heated copper and others boiled under pressure by circulating the wort through a plate heater. The latter method gave a robust palate and higher stability with strong beers, but with weak beers the advantage may not be so marked.

The effect of yeast pitching rate on lager fermentations has been investigated in a pilot plant by E. Helm and B. Trolle.<sup>229</sup> Although the rate of fermentation varied with pitching rates between 0.5 to 2.3 lb. per barrel, the character, composition, and stability of the finished beers were not affected.

R. Schneider<sup>230</sup> discusses the relative merits of open and closed fermenting vessels for lager beer and decides that all such vessels should be covered.

Recent developments in malting, brewery and bottling plant and layout in the U.S.A. and Scandinavia are described by C. J. Virden and J. L. McCowen.<sup>231</sup>

A modern mechanised bottling store in this country is briefly described in the *Brewers' Journal*.<sup>232</sup> Bottle-washing detergents are considered by T. S. Bremner and H. E. Kelly,<sup>233</sup> and a new one is described by O. M. Morgan.<sup>234</sup> A general consideration of the process of bottling is contained in a series of articles by the late Lloyd Hind published in the *Journal of the Incorporated Brewers Guild*.<sup>235</sup> W. J. Watkins has described the pre-bottling flash pasteurisation of beers followed by bottling under sterile conditions.<sup>236</sup>

Centrifugal sludge separation from worts and beers is dealt with by E. Helm,<sup>237</sup> R. H. Dolton,<sup>238</sup> R. Laneau,<sup>239</sup> and R. de Wilde.<sup>240</sup>

Beer filtration with the Metafilter is described by J. A. Pickard,<sup>241</sup> and laboratory tests for the permeability and efficiency of filter pulp have been carried out by L. A. van Gastel and H. van Veldhuizen.<sup>242</sup>

Laboratory tests on two grades of commercial aluminium and three of aluminium alloys were made by contact with beer for four weeks. At 4° C. no significant difference was detected, at 25° C. pure aluminium and aluminium alloy anodised in sulphuric acid were the most satisfactory.<sup>243</sup>

Beer and wine attack cadmium-plated vessels rapidly at ordinary temperatures and become highly toxic before any alteration in flavour occurs.<sup>244</sup>

A plant for the continuous production of beer has been described by A. L. Mahchenko.<sup>245</sup>

The production of beer from whey was carried out in Germany during the war.<sup>21,246</sup>

V. Salac has contributed a paper on the correction of the composition of brewing water with Wofatit synthetic resins.<sup>247</sup> V. Berglund has given a full and interesting summary of the historical development of the correction of brewing waters and their effect on beer flavour. He has used X-ray analysis to show that the calcium salt deposited on boiling is not, as previously believed,  $\text{Ca}_3(\text{PO}_4)_2$ , but hydroxyapatite  $[\text{3Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2]$ .<sup>248</sup>

Casks for beer are a serious problem in all countries at the present time. E. Urion and P. A. Caron<sup>249</sup> review the merits and defects of casks made from resin-bonded plywood, stainless steel, aluminium, and mild steel lined with aluminium. Further references will be found in B.I.O.S. Final Report No. 1512.<sup>21</sup>

### *Scientific*

An important contribution to our knowledge of the behaviour of proteins in brewing has been made by E. Sandegren.<sup>250</sup> Previous Swedish investigations had shown that albumin and hordein of barley are monodisperse proteins, but that the globulin contains four components ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ). The latter is missing from malt, while only the  $\beta$  component is found in wort as it is resistant to heat and proteolytic enzymes. The chill haze of beer has been isolated by Sandegren and shown to consist of 60–65% protein originating from  $\beta$ -globulin and 35–40% tannin, giving a molecular weight around 40,000. This compound is susceptible to oxidation, particularly in light. Its removal does not affect the head retention of beer.

By fractional precipitation with ammonium sulphate J. H. St. Johnston has isolated four protein-containing fractions from wort. Details are given of their properties and behaviour throughout the brewing process.<sup>250a</sup>

The Swedish work showed that bentonite adsorbed the  $\beta$ -globulin and L. Wallerstein<sup>251</sup> has claimed the addition of bentonite and similar silicates of the montmorillonite type, in conjunction with proteolytic enzymes, as a means of chill-proofing beers.

The effect of light in producing "sun-flavour" in beers contained in bottles of different colours has been investigated by B. Jacobsson and B. Högberg.<sup>252</sup>

The influence of various amounts of air in bottled beers was studied by P. P. Gray, I. Stone, and L. Atkin.<sup>253</sup> By statistically controlled tasting tests it was shown that the effect of the air on flavour is not apparent immediately after pasteurisation but develops on storage more rapidly at high than at low temperatures.

L. Atkin and P. P. Gray<sup>254</sup> have carried out an investigation on the effect of inorganic ions, vitamins, sugars, and yeast extract on the rate of fermentation of yeast at 30° c. for three hours. They used a synthetic medium to which the additions were made, but took care to check that this gave at least as good a fermentation rate as malt wort. In the most satisfactory synthetic solution brewers' yeast showed no response to aneurin in contrast to bakers' yeast.

E. Sandegren<sup>255</sup> has studied the amounts of phytin in barleys, malts, and worts, and found that the content in barleys may vary with the growing conditions. During malting, 20–30% is decomposed. In mashing, a further 60–65% breaks down, the remainder being removed in the spent grains. Addition of lactic acid in mashing increases the proportion of phytin split; while addition of sodium chloride, by cation exchange with calcium and magnesium, increases the proportion rendered soluble.

A large number of analytical results obtained during investigations on the nitrogen fractions of worts and their beers were examined by B. A. Burkhardt and A. D. Dickson.<sup>256</sup> Good correlation was found only between total soluble nitrogen in wort and total soluble nitrogen in beer, as well as between total and formol nitrogen in beer.

A summary of our present knowledge of melanoidins, the complex colouring matters produced by the interaction of amino acids and sugars, has been given by J. Cazier.<sup>257</sup>

J. de Clerck has shown clearly the interesting effect of the redox potential on the solubility of iron in beer. Beer maintained out of contact with air has no effect on iron, but the introduction of air leads to a proportionate increase in the amount of this metal dissolved. Variations in  $p_H$  have comparatively little effect, although acidity slightly increases the amount of iron dissolved.<sup>258</sup>

### *Micro-biological control*

Methods for determining presence of deleterious organisms in brewery plant and various liquids such as water, priming, caramel, etc., are described by W. A. Whitley.<sup>259</sup>

A. Lund describes procedures adopted for determining any sources of infection in the brewery and bottling plant and summarises the methods adopted by various workers for ascertaining the behaviour of yeast by laboratory tests. For the purification of yeast, washing with dilute sulphuric acid at  $p_H$  3 for six hours, as adopted at the Tuborg brewery, is recommended, the acid then being neutralised with sodium hydroxide to produce flocculation.<sup>260</sup>

A procedure for biological sampling of wort and beer with aseptic technique is outlined by J. J. Olshausen.<sup>261</sup>

Sanitation in beverage plants is described by S. S. Epstein.<sup>262</sup> Equipment should be designed to be readily taken apart and sterilised with steam, hot water, Cl solutions, or non-corrosive, non-toxic disinfectants. Ultra-violet irradiation may be very useful for reducing contamination at various points in the plant. Sampling of water, wort, beer, bottles, and crown corks is described and the compositions of suitable media are given.

## Industrial fermentations

### *Alcohol production*

The enormous expansion in the production of alcohol in the U.S.A. during the war is reflected in a number of studies aimed at obtaining the maximum yield. A general summary of the position is given by C. S. Boruff and J. M. van Lanen,<sup>263</sup> and by W. H. Stark, P. Kolachov, L. A. Smith, H. C. Blankmeyer, and H. F. Willkie.<sup>264</sup>

One development is the use of a continuous process. W. L. Owen<sup>265</sup> describes a laboratory apparatus employing a closed system with decks on which the yeast settles. A 2-bushel-a-day plant for farm use is described by W. B. Altsheler, H. W. Mollet, E. H. C. Brown, W. H. Stark, and L. A. Smith.<sup>266</sup> E. W. Ruf, W. H. Stark, L. A. Smith, and E. E. Allen<sup>267</sup> find that, for the continuous process, the acid conversion of maize is better than malt mashes. The addition of mould bran or *Aspergillus oryzae* cultures prevented yeast degeneration. The value of proteolytic enzyme additions was shown to be that of supplying nitrogenous yeast nutrients.<sup>268</sup>

Alcohol production from other sources has been investigated. *Torulopsis utilis* can ferment the hexoses of waste sulphite liquor and utilize the pentoses for growth.<sup>269,270,271</sup>

Production of alcohol from artichokes<sup>272</sup> and from grape stems<sup>273</sup> has been described.

### *Other industrial fermentations*

A considerable number of papers have appeared on the production of 2:3-buteneglycol by fermentation processes because of its employment in the production of synthetic rubber, but a wide variety of other uses is envisaged. A full historical summary is given by L. A. Underkofler and E. I. Fulmer<sup>274</sup> with references up to 1947 and a summary of the numerous organisms employed by different investigators. Production using two selected types of *B. subtilis* is described by A. C. Blackwood, A. C. Neish, W. E. Brown, and G. A. Ledingham.<sup>275</sup> The use of *B. polymyxa* has been studied by D. Rose<sup>276</sup> and by H. Katznelson<sup>277</sup>; whilst

production using *A. aerogenes* is the subject of papers by G. G. Freeman<sup>278</sup> and by W. Stark, S. L. Adams, P. Kolachov, and H. F. Willkie.<sup>279</sup>

The production of streptomycin by large-scale surface culture has been described by G. C. Ainsworth *et al.*<sup>280</sup> and pilot scale extraction and purification techniques have been developed by T. J. Woodthorpe and D. M. Ireland.<sup>281</sup>

A series of 16 papers has been published on aureomycin.<sup>282</sup> This new antibiotic is produced from *Streptomyces aureofaciens*, an actinomycete. No information is given as to its chemical nature, but it has been obtained as a highly purified, crystalline, faintly golden-yellow substance. It is effective against Gram-positive and Gram-negative organisms and bacteria do not readily become resistant to its action. It has a low toxicity. Laboratory trials are not altogether favourable, nevertheless it has given very promising results in clinical trials, particularly with resistant chronic infections of the urinary tract. Its most striking effects are shown on the viruses and rickettsiae for, although it has no apparent action *in vitro*, it exhibits marked therapeutic activity against the viruses of the psittacosis-lymphogranuloma group and rickettsiae of the spotted fever, typhus fever, scrub fever, and Q fever groups. It therefore appears to have a somewhat similar range of action to that of chloromycetin from *Streptomyces venezuelae*.<sup>283, 284</sup>

### Insect pests

The occurrence and life history of the Khapra beetle (*Trogoderma granarium*) are described together with its effects upon infested malt and control measures which have proved effective for its elimination.<sup>285</sup>

A simple and effective method of dispersing DDT as an insecticide consists in igniting a mixture of DDT, sugar, and potassium chlorate, in a tin-plate container the proportions being arranged to give as low a temperature of combustion as possible. The insecticide is converted to a cloud which deposits on all accessible surfaces.<sup>286</sup>

V. A. Beckley<sup>287</sup> has stated that sacks treated with a mixture of pyrethrum powder and diatomite, in contact with weevily wheat, remained almost free from living weevils for a period of about eight months, whilst wheat in untreated sacks showed about 57% of damaged grains.

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## MEDICINAL SUBSTANCES

By N. R. CAMPBELL, B.Sc., Ph.D., A.R.I.C.

*Allen and Hanburys Limited*

THIS year, with more space made available for this section, an attempt has been made to give somewhat fuller accounts of interesting work and trends of work in particular sub-sections. It is difficult to strike a reasonable mean between reciting a catalogue of scientific papers and committing the grievous error of missing an item of interest to a reader; the tendency, perhaps regrettably, is in the former direction. Armed with a reference, the individual may examine a paper at his leisure.

The interest shown at the present time in the subject of the liver factors which cure pernicious anaemia, is so great, that it was decided to devote an unusually large amount of space to its consideration. Accordingly, since the vitamin A group has also received much attention this year, various references to vitamins and growth factors in other groups have been omitted.

Much useful, systematic research in the antimalarial field has been published this year and there is a growing number of publications concerned with the chemotherapy of tuberculosis. The impossibility of attending to everything must be accepted as the excuse for their absence from this review.

### Antibiotics

*Penicillin.*—The most important practical advance in the penicillin field during the year is probably the introduction of procaine penicillin, which has been described by a group of American workers in the Lilly Research Laboratories and the Lilly Laboratories for Clinical Research,<sup>1</sup> as a sparingly soluble penicillin containing 90% benzylpenicillin and forming oil suspensions of suitable particle size for slow release of penicillin over prolonged periods. This has previously been achieved by injection of the usual penicillin suspension in oil and wax, which is associated with undesirable local reactions.

The same material has been described in more detail, and apparently independently by workers in the research laboratory of Chas. Pfizer and Co.<sup>2</sup> This paper describes the procaine salts of benzylpenicillin and *n*-amylpenicillin.

G. T. Barry, Y. Sato, and L. C. Craig<sup>3</sup> have made a study of the distribution of crystalline penicillins over a range of solvent systems with a consequent study of the stability of various penicillins in the solvent systems under consideration. The same workers, using the method of counter-current distribution, have obtained crystalline benzylpenicillin containing radioactive sulphur; this was isolated from crude amorphous penicillin obtained by extraction of a culture of *P. notatum* grown in a medium containing radioactive sulphur, as sodium sulphate. Radioactive penicillin with a much higher specific activity has also been made by a composite team working in this country.<sup>4</sup>

A considerable amount of work has been carried out on the subject of precursors in the biosynthesis of penicillin. A long and interesting series of papers has been published by workers in the Lilly Research Laboratories. The first of these<sup>5</sup> deals with biological precursors for benzylpenicillin, using strain NRRL 1976; among many positive results perhaps the two most interesting are the notable efficacy of N-crotyl phenylacetamide and the fact that benzylpenicillin is formed when N-(2-hydroxyethyl)- $\gamma$ -phenylbutyramide is used as precursor. This latter demonstrates that the mould can degrade phenylbutyryl compounds by the loss of two carbon atoms.

The second<sup>6</sup> describes the preparation of deuterophenylacetyl-N<sup>15</sup>-DL-valine and its use as a precursor; results have shown that the phenylacetyl portion was incorporated directly into the molecule but, in contrast, very little N<sup>15</sup> was found in the penicillin resulting. The third<sup>7</sup> describes methods generally, and gives the results obtained by the use of a great variety of aliphatic, aromatic, and arylaliphatic acids as precursors, while the fourth<sup>8</sup> gives an account of the isolation and identification of about 30 new penicillins. In certain cases the mould appeared to have formed the new penicillin with exclusion of the natural penicillin; the highest recorded activity against *S. aureus* for one of these new penicillins is shown by *n*-butylmercaptomethylpenicillin, active to the extent of 3400 units per milligram.

With a change of journal, the series continues with two papers<sup>9,10</sup> on the use of N-2-hydroxyethylamides of various acids and proceeds to a paper<sup>11</sup> on hydroxy- and mercapto-acetic acids with certain of their derivatives; the mercaptoacetic acids have been found particularly well utilised by penicillin-producing moulds and to be valuable precursors for the preparation of aliphatic type penicillins, difficult to prepare otherwise.

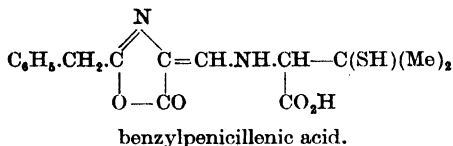
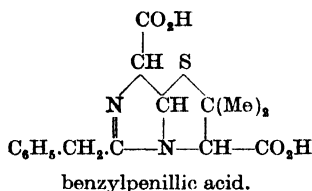
A group of workers in the Upjohn Research Laboratories<sup>12</sup> have prepared  $\gamma$ -chlorocrotylmercaptomethylpenicillin by the use of the appropriate substituted acetic acid as precursor.

F. H. Carpenter<sup>13</sup> has prepared the anhydride of benzyl-penicillin by the use of thionyl chloride and pyridine, and has used the anhydride to prepare the methyl and  $\beta$ -dimethylaminoethyl esters by reaction with the appropriate alcohol. H. Adkins and co-workers have "desulphurised" benzyl-penicillin under conditions so mild as to afford good evidence that the formation of desthiobenzyl-penicillin proceeds without intramolecular rearrangement.<sup>14</sup>

N. R. Trenner and R. P. Buhs<sup>15</sup> have claimed the preparation of a crystalline form of benzyl-penicillinic acid containing one mole of diisopropylether of crystallisation per mol. of benzyl-penicillin; they consider that the material is not the possible oxonium salt but that the ether merely permits the formation of a well-defined crystal-lattice.

Two papers dealing with the synthetic side of the work on penicillin have been published by du Vigneaud and his colleagues at the Biochemistry Department, Cornell University Medical College. The first<sup>16</sup> is an account of work done before 1946 on the synthesis of (-)-benzylpenillioic acid in 19% yield by condensation of (-)-penicillamine hydrochloride with

2-benzyl-4-methoxymethylene-5(4)-oxazolone, while the second<sup>17</sup> follows this up with the preparation, in good yield, of ( $\pm$ )-benzylpenillic acid from crystalline ( $\pm$ )-benzylpenicillenic acid, thus obtaining strong evidence for the theory that the latter is an intermediate in the former synthesis. The further interesting fact emerges that when crystalline ( $\pm$ )-benzylpenicillenic acid is heated in pyridine antibiotic activity is produced which is quantitatively comparable with that obtained by the condensation of ( $\pm$ )-penicillamine hydrochloride with 2-benzyl-4-methoxy-5(4)-oxazolone.



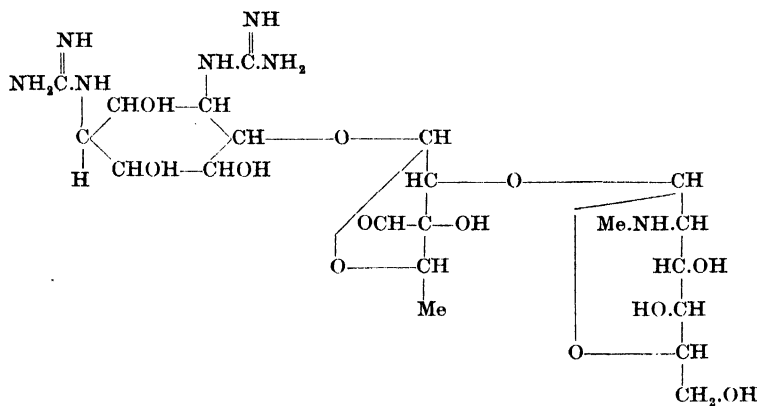
*Streptomycin*.—S. A. Waksman<sup>18</sup> has suggested a new nomenclature for streptomycin preparations. The chief constituent of the generally known mixture, from degradation studies recognised as having the structure of an O-glycoside of streptobiosamine (N-methyl-L-glucosaminidostreptose) with streptidine (1:3-diguanido-2:4:5:6-tetrahydroxycyclohexane), is to be called Streptomycin. The entity formerly known as streptomycin B and now chemically defined as D-mannosido-N-methyl-L-glucosaminidostreptosido-streptidine, is to be called Mannosidostreptomycin. The term Streptomycin Complex is to be used for the group of antibiotics, derived from *S. griseus*, exhibiting the characteristic antibacterial spectrum and chemical and physical properties of streptomycin, while Streptomycin Residue is to be used for the residue left after removal of highly purified streptomycin from impure preparations. The expression Streptomycin-like Substances is to be used to imply any preparations produced by organisms other than *S. griseus* showing the antibiotic spectrum and properties characteristic of streptomycin.

L. J. Heuser, M. A. Dolliver, and E. T. Stiller claim to have made the first preparation of the crystalline trihydrochlorides of streptomycin and mannosidostreptomycin.<sup>19</sup>

Degradation studies on streptomycin are proceeding; O. Wintersteiner and A. Klingsberg<sup>20</sup> have degraded O-tetramethyl-streptamine to DL-dimethoxysuccinic acid. M. L. Wolfrom and W. J. Polglase,<sup>21</sup> of the Chemistry Department, Ohio State University, have made a preliminary report of their synthesis of streptidine from hexacetyl-streptamine (previously synthesised from D-glucosamine) via the reaction of streptamine sulphate with S-methylthiopseudo-urea sulphate to yield streptidine sulphate monohydrate.

R. L. Peck, F. A. Kuehl, C. E. Hoffhine, E. W. Peel, and K. Folkers<sup>22</sup> have benzoylated streptomycin to the undecabenzoyl derivative, and dihydrostreptomycin to the dodecabenzoyl derivative; both of these were split by hydrobromic acid to heptabenzoylstreptidine and hydrolysis of this yielded streptidine, showing that no change in structure occurs

during the cleavage of streptomycin with acid. Since heptabenzoyl-streptidine on oxidation gave more than one equivalent of dibenzoyl-guanidine it is concluded that streptobiosamine is linked to streptidine through an oxygen atom. Following the conclusion that streptose is 3-C-formyl-L-lyxomethylose, which is supported by M. L. Wolfrom and C. W. de Walt,<sup>23</sup> and that streptobiosamine is attached to C4 of streptidine (supported by M. L. Wolfrom and W. J. Polglase),<sup>24</sup> K. Folkers and his colleagues in the Research Laboratories of Merck and Co. Inc.<sup>25,26</sup> have suggested the following structure for streptomycin :



E. Titus and J. Fried<sup>27</sup> have obtained evidence, based on counter-current distribution studies, that streptomycin consists of a mixture of tautomeric forms, the relative proportions depending upon  $p_H$ . The tautomers appear to be at least partially separable by chromatography. W. A. Winsten and E. Eigen<sup>28</sup> have carried out paper partition chromatograph experiments on the streptomycin complex and claim to have recognised at least two other antibiotics in addition to the three already known.

T. F. Paine and M. Finland<sup>29</sup> have examined the variants obtained from sensitive strains of the organisms *S. aureus*, *E. coli*, *Ps. aeruginosa* and *Proteus morgani*. In all cases they have isolated strains resistant to streptomycin, and strains dependent upon the drug for growth. While resistant strains bred true in sub-culture it was found possible by repeated sub-culture to interchange sensitivity and dependence more or less at will. R. J. Fitzgerald and F. Bernheim<sup>30</sup> have discovered that the bacteriostatic effect of streptomycin on *E. coli* and on two strains of *M. tuberculosis*, which can be antagonised by a number of purines and pyrimidines, can also be antagonised by urea.

A report on a meeting of the Medical Society of London, held for a discussion on streptomycin, has been reported in the *British Medical Journal*.<sup>31</sup> Accounts are given of its use in tuberculous meningitis, pulmonary tuberculosis, *B. coli* infections, and urinary infection generally.

**Polymyxins.**—Three important papers from the Wellcome Research Laboratories give most of the available information on the subject of "aerosporin" and "polymyxin." The first, by G. Brownlee and T. S. G.

Jones,<sup>32</sup> gives an account of the historical aspect of the matter; the sources of the two antibiotics were shown in 1937 to be identical and the original name for the material discovered by the Wellcome group, "aerosporin"<sup>33,34</sup> has been abandoned in favour of polymyxin A. The polymyxin, described by Stansly *et al.*,<sup>35</sup> is now, by agreement, named polymyxin D.

Both antibiotics are polypeptides, polymyxin A yielding on hydrolysis D-leucine, L-threonine, L- $\alpha$ : $\gamma$ -diaminobutyric acid, and an unidentified, optically active fatty acid of formula  $C_9H_{18}O_2$ ,<sup>36</sup> while polymyxin D has been hydrolysed to give all of these acids with the addition of serine.<sup>37</sup>

The polymyxins A and D suffer from the defect of nephro-toxic properties; we await with interest some account of polymyxins B and E, which are stated to be free from this objection.

The American workers in this field<sup>38</sup> have described the nutritional and environmental factors influencing the production of polymyxin by *B. polymyxa*, and have worked out details of a large-scale laboratory preparation.

According to E. B. Schoenbach, M. S. Bryer, E. A. Bliss, and P. H. Long<sup>39</sup> polymyxin is 5–10 times as active as streptomycin against *K. pneumoniae* and Pfeiffer's bacillus.

*Chloromycetin*.—This is a new antibiotic originally named by J. Ehrlich, Q. R. Bartz, R. M. Smith, D. A. Joslyn, and P. R. Burekholder.<sup>40</sup> R. M. Smith, D. A. Joslyn, O. M. Gruhzeit, W. McLean, M. A. Penner, and J. Ehrlich<sup>41</sup> have found chloromycetin to have notable activity against both Gram-positive and Gram-negative organisms, and have found that the crystalline substance affords remarkable protection against *Rickettsia prowazeki* in chick embryos. The toxicity was found to be of the same order as that of streptomycin.

J. Ehrlich, D. Gottlieb, P. R. Burekholder, L. E. Anderson, and T. G. Pridham<sup>42</sup> have described the source of chloromycetin as a new species named *Streptomyces venezuelae*, very similar to but not identical with *S. lavandulae*, the source of streptothricin, and Q. R. Bartz<sup>43</sup> has given an account of the isolation of chloromycetin from filtrates of submerged aerated cultures. He has obtained the material crystalline and has found it to show remarkable stability to heat in aqueous solution. Analysis showed carbon, hydrogen, nitrogen, and nonionised chlorine; a solution containing 0.2 $\gamma$  per ml. caused 50% inhibition in the growth of *Shigella paradysenteriae* (Sonne), while under the same conditions 10 $\gamma$  of streptomycin base were required for similar effect.

Chloromycetin has been found very promising in clinical tests in scrub typhus and it has been stated that administration of chloromycetin to patients with typhus fever is a relatively safe procedure and that the chemotherapeutic effect is sufficiently encouraging to warrant further tests.<sup>45</sup>

*General and miscellaneous*.—Under the title "Recent Advances in Antibiotic Research," P. P. Regna has given an interesting account of the historical aspect of penicillin and streptomycin.<sup>46</sup>

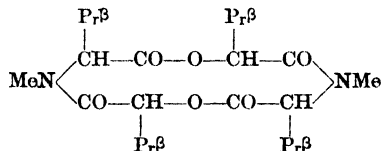
L. C. Craig and his collaborators at the Rockefeller Institute for Medical Research have applied their most important counter-current distribution technique to the study of gramicidin<sup>47</sup> and of bacitracin.<sup>48</sup> The former

has been separated into gramicidin A and B and at least two other components have been indicated. Bacitracin has been similarly examined and a preliminary report made on an amino acid analysis on the products of its acid hydrolysis.

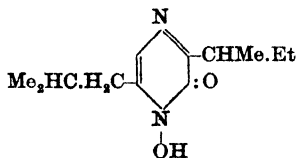
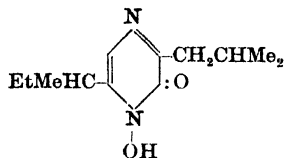
A useful account has been published by R. K. Callow, R. E. Glover, P. D. Hart, and G. M. Hills (in 1947)<sup>49</sup> describing bacteriological tests on, and details of preparation of, licheniformin. This substance is a base, extracted from *B. licheniformis* culture media by adsorption on carbon and conversion to suitable salts. It has considerable bacteriostatic activity against a number of species, but is of interest particularly in its effect on *M. tuberculosis*. It shows strong synergism with sulphathione (tetrasodium salt of 4:4'-bis-( $\gamma$ -phenyl-*n*-propylamino-diphenylsulphone  $\alpha:\gamma:\alpha':\gamma'$ -tetrasulphonate). In this it resembles streptomycin.<sup>50</sup> Licheniformin has unfortunately rather high toxicity.

J. H. Ford and B. E. Leach have described actidione,<sup>51</sup> a new antibiotic from streptomycin-producing strains of *S. griseus*; methods for its isolation and purification have been given, together with analytical data. Actidione has little or no activity against bacteria, but is very effective against many yeasts.

Pl. A. Plattner and co-workers<sup>52</sup> have isolated enniatins A and B from cultures of *Fusarium orthoceras* var. *enniatum*. Both show activity against *M. paratuberculosis* and *M. phlei*, enniatin A being much more active than B in the former case. On the basis of degradation studies the following most interesting structure has been proposed for enniatin B.<sup>53</sup>



Two alternative structures for aspergillic acid have been given by G. Dunn, G. T. Newbold, and F. S. Spring.<sup>54</sup>



A new antibiotic from a strain of *B. subtilis* has been described by C. H. Hassell<sup>55</sup>; this substance, subtilin C, appears to be a polypeptide and is effective in high dilution against most Gram-positive organisms tested.

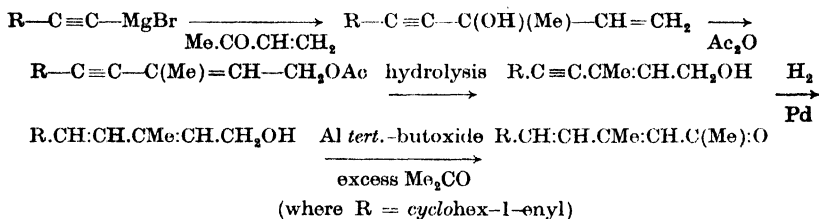
## Vitamins and growth factors

**Vitamin A group.**—Sir I. Heilbron,<sup>56</sup> in the Pedler Lecture, delivered before the Chemical Society in December 1947, has given a most interesting account of the historical course of the isolation and synthesis of vitamin A. He has also indicated the lines on which his research school is pursuing further synthetic work in this field.

E. M. Shantz<sup>57</sup> has claimed the isolation of pure vitamin  $A_2$  as a viscous orange-yellow oil separated as the crystalline phenylazobenzoate, but not itself crystallisable. While admitting that his evidence throws little light on the structure of the vitamin this author is inclined to give slight preference to the structure proposed by Karrer *et al.*<sup>58</sup>

Ethers of vitamin  $A$  and of related compounds have attracted considerable attention: crystalline vitamin  $A$  methyl ether has been prepared by the action of methyl sulphate upon the lithium salt of the vitamin alcohol.<sup>59</sup> The research group working under N. A. Milas at the Massachusetts Institute of Technology have published the complete synthesis of four biologically active vitamin  $A$  ethers,<sup>60</sup> the methyl and ethyl ethers in a state of purity and the isopropyl and *tert.* butyl much less so. The 4-alkoxybutan-2-ones were employed as starting materials and the key intermediate for several routes was 1(2': 6': 6'-trimethyl-*cyclohexen*-1'-yl)-3-methylbut-1-en-4-al. The same group has published at the same time the synthesis of homovitamin  $A$  ethyl ether and of 5-dehydro-homovitamin  $A$  ethyl ether; crude preparations of both of the latter were found to possess anti-xerophthalmic (vitamin  $A$ ) activity. A separate paper<sup>62</sup> deals with the application of the Darzens reaction to  $\beta$ -ionone as a means for obtaining the key intermediate mentioned above. Milas' synthesis of vitamin  $A$  is the subject of a patent abstracted during the year but originally dated 1944.<sup>63</sup>

Following the announcement of a new approach to vitamin  $A$  synthesis in 1947,<sup>64</sup> N. A. Milas, F. X. Grossi, S. E. Penner, and S. Kahn<sup>65</sup> have synthesised the ketone 1(*cyclohexene*-1-yl)-3-methyl-1:3:5-octatriene-7-one by the method depicted below:



P. Karrer and J. Benz<sup>66</sup> have synthesised axerophthene by dehydration of the ethyl tertiary carbinol obtained by the reaction of lithium ethyl with the " $\text{C}_{18}$  ketone." P. Karrer and R. Schweizer<sup>67</sup> have dehydrated vitamin  $A$  via the toluene sulphonic ester and sodium iodide to anhydro-vitamin  $A$  (80-90% crude yield), obtaining as a by-product a reddish-yellow pigment which appeared to contain  $\beta$ -carotin (4%). Anhydro-vitamin  $A$  on partial catalytic reduction yielded axerophthene, with other products. The axerophthene type of structure has also been obtained, in the form of desmethyl-axerophthene, by P. Karrer and J. Benz,<sup>68</sup> who have dehydrated the dimethyl tertiary carbinol obtained from the reaction of excess lithium methyl with  $\beta$ -ionylidenecrotonic acid. The same authors<sup>69</sup> have condensed  $\beta$ -ionone with acetylene in liquid ammonia and partially reduced the resulting alcohol to give 1:1:5-trimethyl-5-hydroxy-6-(3'-methylpentadiene-2': 4'-ylidene)-*cyclohexane*.

H. B. Henbest<sup>70</sup> has reported the preparation of dehydro  $\beta$ -ionone from  $\beta$ -ionone by the use of N-bromosuccinimide.

*Folic acid—Lactobacillus casei factors.*—T. H. Jukes and E. L. R. Stokstad have given a very complete account of pteroylglutamic acid and related compounds up to the beginning of the year,<sup>71</sup> from both chemical and pharmacological points of view. This should not be missed by those interested in the subject and it may be regarded as paving the way to the appreciation of a series of papers from the Lederle laboratories and Calco Chemical Divisions of the American Cyanamid Company.

The first of these<sup>72</sup> is on the subject of the fermentation *L. casei* factor which is obtained from aerobic cultures of an unidentified organism believed to be a corynebacterium, and which is distinguished by analysis and biological activity from any similar compound previously reported. The second paper<sup>73</sup> describes the isolation of the *L. casei* factor from liver, while the third and fourth<sup>74</sup> deal with the degradation of the fermentation *L. casei* factor. The essentials of this work were reported in this article in the 1946 volume, but the subject is considered of sufficient importance and interest to be worthy of some detailed attention.

Anaerobic alkaline hydrolysis of the fermentation factor gave the optically inactive modification of the liver factor together with 2 mols. of a dicarboxylic  $\alpha$ -amino acid; aerobic alkaline hydrolysis gave 2-amino-4-hydroxypteridine-6-carboxylic acid and an aromatic amine. The aromatic amine obtained from the aerobic alkaline hydrolysis of the racemic liver factor consisted of a dipeptide of *p*-aminobenzoic acid and an  $\alpha$ -amino acid; anaerobic acid hydrolysis of the fermentation factor yielded 2-amino-4-hydroxy-6-methyl pteridine. The linkage of the pteridin to the amino group of *p*-aminobenzoic acid was inferred.

The second of these two papers on the degradation work reports the isolation of *l*-pyrrolidinecarboxylic acid, 2-amino-4-hydroxy-pteridine-6-carboxylic acid, 2-amino-4-hydroxy-6-methylpteridine and *p*-aminobenzoic acid from the fermentation factor. Paper No. 5<sup>75</sup> returns to the liver factor and establishes the structure of the pteridine nucleus, postulating the now well-known structure for the liver factor (pteroylglutamic acid).

The concluding four papers<sup>76</sup> are concerned with the synthesis of pteroylglutamic acid. The first of these commences with a presentation of the status of the nomenclature of the *L. casei* factors. The expression "folic acid" is discarded as unsuitable for the naming of a definite chemical entity, since the name was first applied to an unidentified factor and is popularly applied to any material with the general type of activity of these factors. The basic name, pteric acid, is applied to 4-[(2-amino-4-hydroxy-6-pteridyl)-methyl]-amino} benzoic acid; the fermentation *L. casei* factor lacks an exact name since the nature of the peptide linkage still required to be elucidated, but Jukes and Stokstad<sup>71</sup> have apparently accepted the term pteroyltriglutamic acid used by J. O. Lampen and M. J. Jones.<sup>77</sup> The names pteroylhexaglutamylglutamic acid or pteroyl-heptaglutamic acid are used for the "vitamin B conjugate."

Pteroylglutamic acid was prepared in the form of crude products containing the acid to the extent of about 20% by reaction between 2:4:5-triamino-6-hydroxypyrimidine, *p*-aminobenzoylglutamic acid

and  $\alpha$ : $\beta$ -dibromopropionaldehyde. A second synthesis of pteroylglutamic acid and of pterioic acid employs the N-[(2-amino-4-hydroxy-6-pteridyl)-methyl] pyridinium iodide prepared by the reaction of N-(2-formyl-2-bromoethyl)-pyridiniumbromide with 2:4:5-triamino-6-hydroxypyrimidine; this is used to alkylate the appropriate amino acid.

The third paper of the "synthesis" series presents a very interesting use of reductone (2:3-dihydroxyacrylaldehyde) as a three-carbon compound forming a stable intermediate by reaction with *p*-aminobenzoylglutamic acid. In practice these workers have prepared the intermediate by reaction of reductone with the diethyl ester of *p*-aminobenzoylglutamic acid and then brought the product into further reaction with 2:4:5-triamino-6-hydroxypyrimidine. This synthesis has called forth comment from H. S. Forrest and J. Walker,<sup>78</sup> of the National Institute for Medical Research, who have approached this synthesis from biochemical considerations of the possibility of reductone being stabilised in the bacterial cell by the presence of *p*-aminobenzoic acid<sup>79</sup> and the linked components being then incorporated into pterioic acid and similar factors. They have prepared pterioic acid by interaction of the reductone-methyl *p*-aminobenzoate compound with 2:4:5-triamino-6-hydroxypyrimidine.

The last paper of the group describes a new synthesis of 2-amino-4-hydroxy-6-methylpteridine and the synthesis, from a halogenated derivative of this with diethyl *p*-aminobenzoylglutamate, of pteroylglutamic acid.

The American Cyanamid group have continued their investigations into the exact structure of the fermentation *L. casei* factor; the first two papers<sup>80</sup> of a new series on pterioic acid derivatives describe the preparation of pteroyl- $\alpha$ -glutamylglutamic acid, pteroyl- $\alpha$ : $\gamma$ -glutamyl-diglutamic acid, pteroyl- $\gamma$ -glutamylglutamic acid and pteroyl- $\gamma$ -glutamyl- $\gamma$ -glutamylglutamic acid. The second of these was found to be not identical with the fermentation *L. casei* factor but the fourth, though not isolated from the reaction-mixture, was found to have the same ratio of activity for the two test organisms, *S. faecalis* R. and *L. casei*, as does the fermentation factor.

P. Karrer and R. Schweizer<sup>81</sup> have described another synthesis of pteroylglutamic acid; a product containing 15% of required product was obtained by reaction between *p*-aminobenzoylglutamic acid and the condensation product from dihydroxyacetone and 2:4:5-triamino-6-hydroxypyrimidine. Active material was also obtained by allowing the same triaminohydroxypyrimidine to react with *p*-aminobenzoylglutamic acid and glyceraldehyde di-toluenesulphonic ester.

M. Gordon, J. M. Ravel, R. E. Eakin, and W. Shive<sup>82</sup> have prepared the formyl derivative of pteroylglutamic acid; this was found to be as effective as the parent acid in growth-stimulating experiments, but approximately 30 times as active in preventing the toxicity of 7-methylpteroylglutamic acid as an inhibitor for *S. faecalis*. Synthetic rhizopterin was found to be two to three times as effective as pteroylglutamic acid in preventing the toxic effects of this inhibitor, while in its turn methyl pteroylglutamic acid had its toxicity increased several times by treatment with 98% formic acid. The activity of rhizopterin indicates that it is

probably converted directly to formylfolic acid. This, together with other, as yet unpublished, work offers additional evidence that the biochemical function of *p*-aminobenzoic acid and pteroylglutamic acid derivatives involves the introduction of a single carbon unit into purines, pyrimidines, and possibly histidine.

E. Lester Smith<sup>83</sup> has obtained two red pigments from ox-liver extracts which he believes to be the true anti-pernicious anaemia factor, in two forms. This factor has an effective dose of possibly less than 20  $\mu$ g. daily.

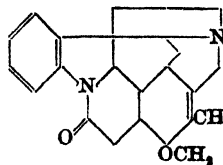
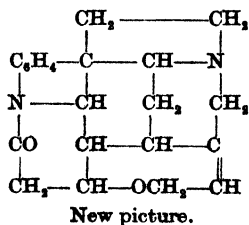
The above announcement is somewhat overshadowed by the isolation of crystalline "vitamin B.12" by K. Folkers and his collaborators in the Research Laboratories of Merck & Co. Inc.<sup>84</sup> This material has been isolated from liver and is claimed to produce positive haematological response when given in micro-gram quantities to patients with Addisonian pernicious anaemia; it is described as crystallising in small red needles and has also been isolated from the culture medium of a strain of *Streptomyces griseus*.

W. Shive, R. E. Eakin, W. M. Harding, J. M. Ravel, and J. E. Sutherland<sup>85</sup> have isolated a crystalline factor from pig-liver which was found to be several times as active as pteroylglutamic acid in preventing the toxic action of methylpteroylglutamic acid upon the growth of *Leuconostoc mesenteroides*. This has been identified as thymidine.

Although published in 1947 it is considered desirable to include a brief review of the literature on rhizopterin, in view of the quantity of important work on the subject of pteroylglutamic acid and related factors carried out or published during 1948. Three papers from the research laboratories of Merck and Co. Inc. have described the isolation,<sup>86</sup> degradation,<sup>87</sup> and structure<sup>88</sup> of rhizopterin; it is highly active as a growth-factor for *Streptococcus lactis* but not so for *Lactobacillus casei*. The best known source is the fumaric acid fermentation liquors from *Rhizopus nigricans* and on first discovery it received the title "S.L.R. factor" (*S. lactis* R.). Degradation and physical studies, followed by synthesis, have shown that rhizopterin is N-formyl-pterotic acid.

## Alkaloids

*Strychnos alkaloids*.—The general impression is to be gained from the literature that, despite the somewhat revolutionary suggestion made by (Sir) R. Robinson and reported last year, the proposed structure reported the previous year (Robinson and Openshaw) has met with widespread approval. This structure is now represented on paper by a "square" picture which, mercifully, lacks the somewhat ungainly aspect of the original picture.



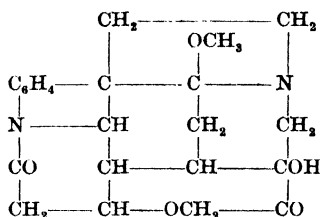
Old picture.

R. B. Woodward and W. J. Brehm,<sup>89</sup> Harvard University, having shown that the neo-bases derived from the strychnos alkaloids contain

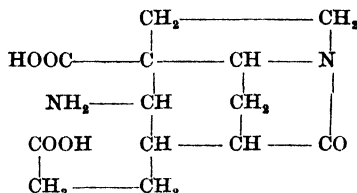
the part structure  $\begin{array}{c} | \\ -N-CH=C-C, \\ | \\ C \end{array}$  now consider that previous difficulty

in the way of the structure above are resolved.

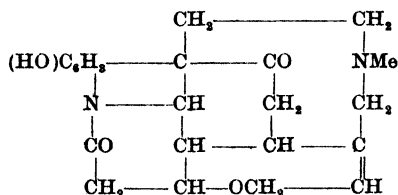
A. S. Bailey and R. Robinson<sup>90</sup> have described the conversion of the N-oxide of strychnine to *pseudostrychnine* (hydroxystrychnine) by treatment with aqueous potassium chromate as the best process available. V. Prelog and A. Kathriner<sup>91</sup> have oxidised *pseudostrychnine* with dilute acid aqueous permanganate and obtained a compound  $C_{22}H_{24}O_5N_2$  to which the structure below is given :



V. Prelog and M. Kocor<sup>92</sup> have degraded strychnine to an aminodicarboxylic acid which retains the F and G rings of strychnine :



A. S. Bailey and R. Robinson in the course of work on the relation of vomicine to strychnine and brucine have oxidised vomicine with chromic acid to yield an acid which has also been obtained by the oxidation of N-methyl-*sec.pseudostrychnine* or of N-methyl-*sec.pseudobrucine*. A structure for vomicine advanced on several grounds is shown below :

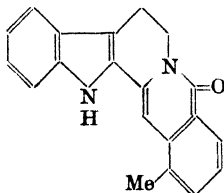


*Colchicine*.—Windaus<sup>94</sup> originally suggested structure for colchicine requires ring C to be six-membered whereas the structure more recently proposed by Dewar<sup>95</sup> requires it to be seven-membered. H. R. V. Arnstein, D. S. Tarbell, H. T. Huang, and G. P. Scott<sup>96</sup> have oxidised

hexahydrocolchicine with periodic acid, a little less than 1 mol. being taken up to yield an aldehyde. Since, according to Dewar's structure hexahydrocolchicine would be a 1:2-glycol this result gives most desirable experimental support to the seven-membered ring hypothesis. Windaus' structure requires hexahydrocolchicine to be a 1:3-glycol which would not be expected to undergo oxidation with periodate.

*Sparteine*.—N. J. Leonard and R. E. Beyler<sup>97</sup> have reported a convenient synthesis of sparteine; ethyl 2-pyridyl acetate was condensed with ethyl orthoformate to yield 1-carbethoxy-4-keto-3-(2'-pyridyl)-pyridocoline, which was then submitted to reductive cyclisation (hydrogenation over copper chromite). In view of this claim to a sparteine synthesis G. R. Clemo, R. Raper, and W. Short<sup>98</sup> have wished to place on record their reduction of L-oxysparteine to L-sparteine by means of lithium-aluminium hydride. They claim that the structure of sparteine was completely established as the result of work carried out in their laboratories (Kings College, University of Durham).

*Yohimbine*.—One of the outstanding problems in the chemistry of yohimbine has been the question of the structure of ketoyobyrine, obtained as a neutral product of the selenium dehydrogenation of yohimbine. This has now been shown by R. B. Woodward and B. Witkop<sup>99</sup> to be a lactam derived from carboxyobyrine and to have the following structure:

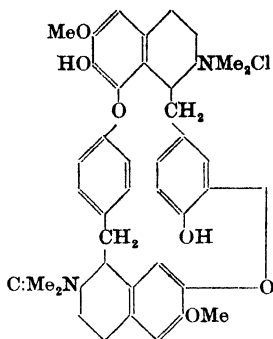


Ketoyobyrine.

The same conclusion has been reached by E. Schlittler and R. Speitel,<sup>100</sup> who have added to these conclusions a synthesis identical in form with a synthesis published by P. L. Julian, W. J. Karpel, A. Magnani, and E. W. Meyer.<sup>101</sup> According to this method tryptamine is condensed with 6-methylhomophthalic acid to N-( $\beta$ -indolyethyl)-6-methylhomophthalimide. This is then converted to the corresponding homophthalic acid, methylated to the ester and cyclised with phosphorus oxychloride to ketoyobyrine.

*Gelsemine*.—B. Witkop<sup>102</sup> has degraded gelsemine to skatole and a base which he considers to be a dimethylisoquinoline. This latter was found to be not identical with any of the three possible dimethylisoquinolines bearing methyl groups only on the pyridine part of the molecule.

*Curare and related alkaloids*.—H. King<sup>103</sup> has determined the structure of (+)-tubocurarine; O-ethylation of (+)-tubocurarine chloride followed by a two-stage Hofman degradation yielded O-ethylbebeerilene, previously obtained from bebeerine. The structure of bebeerine being known, (+)-tubocurarine must have the structure shown below:



D. F. Marsh, C. K. Sleeth, and E. B. Tucker<sup>104</sup> have compared paralysing powers of tubocurarine with the related chondrodendrine and certain derivatives. (+)-N-methylchondrodendrine was found to be about half as active as (+)-tubocurarine in rats and rabbits; (+)-O-methyl-N-methylchondrodendrine showed about the same degree of activity as (+)-tubocurarine but only one-sixth to one-eighth that of (+)-O-methyl-tubocurarine. D. F. Marsh and M. H. Pelletier<sup>105</sup> have made a similar study relative to isochondrodendrine and its derivatives; (+)-N-methyl-isochondrodendrine was found to be about 1/20 and (+)-O-methyl-N-methyl 1/4 as active as (+)-tubocurarine.

*Caffeine and theophylline.*—B. Bobranski and Z. Synowiedski<sup>106</sup> have published details of a synthesis of caffeine used in Poland during the late war. The method is essentially a modified Traube synthesis and in it, cyanacetylurea was converted into the isomeric 4-amino-2:6-dioxyhexahydropyrimidine, nitrosated to iminoviolic acid and this product reduced to the sulphate of the diamine. On formylation with formic acid and sodium formate 4-amino-5-formylamino-2:6-dioxy-pyrimidine was obtained, and isolated. On methylation, caffeine was obtained in an overall yield of 16.5% based on the starting material. The complete synthesis consists of four operations.

The same authors have given a synthesis of theophylline; they found it impossible to prepare it by a method directly analogous to that for caffeine. It was, however, obtained eventually in over 14% yield from the sodium salt of 4-imino-2:6-dioxyhexahydropyrimidine. This was methylated and the product converted to the dimethyliminoviolic acid; as before, this was reduced to the diamine, formylated and cyclised by alkali.

P. Karrer, C. H. Eugster, and O. Ruttner have made a study of emetine and the secondary alkaloids of ipecacuanha and have given an account of the present state of knowledge relative to the still far from solved problem of the structure of these alkaloids. The present position is indicated by partial structures for emetine, emetamine, O-methyl-psychotrine, and dehydroemetine bromide.

### Amino acids and polypeptides

*Amino acid synthesis—general methods.*—Considerable interest has been shown during the year in the use of ethyl  $\alpha$ -acetamidoacetate as

an intermediate in the synthesis of amino acids. The first to publish their results were N. F. Albertson, B. F. Tullar, J. A. King, B. B. Fishburn, and S. Archer,<sup>108</sup> who have prepared the reagent by several methods. These methods include two different reductions of ethyl  $\alpha$ -oximinoacetoacetate, reduction of ethyl acetyloximinoacetoacetate, direct oximation of ethyl acetoacetate followed *in situ* by zinc reduction and from ethyl acetamidomalonate by hydrolysis to the half-ester and acetylation. They have also given examples of its use. R. H. Wiley and O. H. Borum<sup>109</sup> have also prepared the reagent by catalytic reduction of oximinoacetoacetic ester, for which they find the melting point identical with that given by Albertson *et al.* and nearly 100 degrees lower than that reported by Cercez and Colesin.<sup>110</sup>

K. Pfister, C. A. Robinson, A. C. Shabica, and M. Tischler<sup>111</sup> have also prepared and used this reagent; they have prepared it in 88% yield from ethyl acetoacetate by reductive acetylation of ethyl  $\alpha$ -phenylazoacetoacetate. In this paper, which is a preliminary announcement, no mention is made of the melting point of the product; it will be interesting to see this in the full publication. They have hydrogenated the acetamido ester to a mixture containing N-acetyl-DL-*allo*threonine, which crude mixture was then treated with thionyl chloride and the intermediate oxazolone decomposed with water, yielding another crude mixture, of DL-threonine and DL-*allo*threonine containing over 80% of the former. Pure DL-threonine, by this method was obtained in 57% yield from acetoacetic ester.

This thionyl chloride reaction resulting in what these authors refer to as the "oxazoline inversion" is the subject of what can only be described as a "broadside" from D. F. Elliott,<sup>112</sup> who not only claims that the discovery was anticipated by J. Attenburrow, D. F. Elliott, and G. F. Penny,<sup>113</sup> in describing the thionyl chloride method of inverting the configuration of DL-N-benzoyl*allo*threonine ethyl ester and a related method consisting of the treatment of the *p*-toluenesulphonyl derivative with potassium acetate in boiling alcohol, but also claims a third method of obtaining the oxazolone by reaction of DL-threonine ethyl ester hydrochloride with benzimido ethyl ether. D. F. Elliott<sup>114</sup> has also converted DL-serine into inactive cystine by conversion of DL-serine methyl ester hydrochloride into the methyl ester of N-thiobenzoylserine. This on treatment with thionyl chloride gave the thiazoline in almost quantitative yield and on hydrolysis the thiazoline gave a good yield of inactive cystine.

J. Fillman and N. Albertson<sup>115</sup> have prepared  $\gamma$ -hydroxyleucine as an example of a general method of approach to the synthesis of  $\gamma$ -hydroxyamino acids involving condensation of an allyl halide with an acylaminomalonic (or -cyanoacetic) ester, followed by hydrolysis to the lactone and conversion to the amino acid. The same method has been employed by H. L. Goering, S. J. Crystol, and K. Dittmer<sup>116</sup> in the first paper of a new series on the subject of unsaturated amino acids; they have prepared allylglycine, methylglycine, and crotylglycine by reaction of the appropriate allyl chloride with ethyl acetamidomalonate.  $\gamma$ -hydroxyleucine was prepared by acid hydrolysis of ethyl

methallylacetamidomalonate followed by alkaline hydrolysis of the resulting lactone.

J. H. Billman and W. F. Hartung<sup>117</sup> have prepared a number of phthalyl derivatives of amino acids by direct reaction with phthalic anhydride. One particular point in this paper has been taken up by D. A. Kidd and F. E. King,<sup>118</sup> who state that Billman and Hartung's phthalyl derivative from L-glutamic acid must be the DL compound; they have repeated the preparation and find that the crude product has measurable optical activity but consists essentially of the racemic acid (m.p. 189–90°). They claim to have produced authentic phthalyl-L-glutamic acid by reaction of ethyl glutamate with phthalic anhydride followed by thionyl chloride treatment and hydrolysis with dilute acid (m.p. 158–9°).

D. T. Warner and O. A. Moe<sup>119</sup> have described syntheses of amino acids using derivatives of  $\gamma$ -acetamido- $\gamma$ : $\gamma$ -dicarboxybutyraldehyde; the phenylhydrazone of the diethyl ester was found to undergo cyclisation to yield the same product as that obtained by the reaction between gramine and ethyl acetamidomalonate. The cyclised product was converted to DL-tryptophan in the usual way in an overall yield of 50% based on the phenylhydrazone. This same phenylhydrazone on catalytic reduction gave  $\beta$ -acetamido- $\beta$ -carbethoxypiperidone in 70% yield; hydrolysis of this gave an almost quantitative yield of DL-ornithine monohydrochloride.

The same authors have synthesised glutamic acid by oxidation of  $\gamma$ -acetamido- $\gamma$ -carbethoxy- $\gamma$ -cyanobutyraldehyde followed by hydrolysis to the DL-amino acid.

O. Wiss<sup>120</sup> has demonstrated the building-up of alanine from pyruvic acid and ammonium chloride by homogenised liver, in an atmosphere containing oxygen.

*Methionine.*—E. Pierson, M. Giella, and M. Tishler<sup>121</sup> have published a three-step synthesis of methionine. They have repeated the preparation reported last year (Catch, Cook, Graham, and Heilbron) and have found that they could obtain only slightly smaller yields avoiding the undesirable liquid hydrogen cyanide. They prefer the new method:  $\beta$ -methylmercaptopropionaldehyde was prepared from the catalysed addition of methylmercaptan to acrolein at atmospheric pressure, the hydantoin made by the Bücherer reaction and converted to DL-methionine by alkaline hydrolysis.

The enzymatic resolution of DL-methionine has been claimed by C. A. Dekker and J. S. Fruton<sup>122</sup> by the action of papain on a mixture of carbobenzoxy-DL-methionine and aniline.

*Homotryptophan.*—A synthesis of DL-homotryptophan has been effected by H. R. Snyder and F. J. Pilgrim<sup>123</sup>;  $\beta$ -(3-indole)ethyl bromide with ethyl acetamidomalonate gave ethyl  $\alpha$ -acetamido- $\alpha$ -carbethoxy- $\gamma$ -(3-indole)-butyrate which was hydrolysed and decarboxylated to N-acetylhomotryptophan. The acetyl derivative was then hydrolysed to the free amino acid.

*Leucaenine.*—A. F. Bickel<sup>124</sup> has continued his work on this naturally occurring amino acid; having obtained  $\alpha$ : $\beta$ -diaminopropionic acid hydrobromide by bromine oxidation of leucaenine he considers that

its structure may now be regarded as established as  $\beta$ [N-(3-hydroxypyridone-4)]- $\alpha$ -aminopropionic acid.

*p*-Aminosalicylic acid ("PASA").—Considerable interest has been shown during the year in the possibilities of successful use of 4-aminosalicylic acid in the chemotherapy of tuberculosis. C. L. Goodacre, B. W. Mitchell, and D. E. Seymour<sup>125</sup> of the research department of Herts Pharmaceuticals have studied the tuberculostatic activity of the acid together with a long series of derivatives and analogues. The esters were found more or less equally active but to have no marked advantage over the free acid; they have stated as a generalisation that simple substitution appears to give no marked increase in activity.

K. Vennesland, R. H. Ebert, and R. G. Bloch<sup>126</sup> have found an *in vitro* growth of human tubercle bacilli (H-37RV) to be inhibited by 0.74  $\mu$ g./c.c. of streptomycin or by 1.2  $\mu$ g./c.c. of "PASA." *In vitro* growth of a streptomycin resistant strain of human tubercle bacilli (H-37RVNR1) was inhibited by the same concentration of "PASA."

D. D. Martin, F. S. Spring, T. G. Dempsey, C. L. Goodacre, and D. E. Seymour<sup>127</sup> have stated that preparation of *p*-aminosalicylic acid by the reduction of *p*-nitrosalicylic acid is laborious and prefer to prepare it by direct carboxylation of *m*-aminophenol, using modified Kolbé conditions. J. T. Sheehan<sup>128</sup> has prepared the amino acid similarly by the reaction of *m*-aminophenol with ammonium carbonate under pressure, obtaining a yield of 22%. This, however, has been very much improved by H. Erlenmeyer, B. Prijs, E. Sorkin, and E. Suter,<sup>129</sup> who claim yields of 80% from *m*-aminophenol by a Kolbé synthesis with potassium bicarbonate, water, and solid carbon dioxide in an autoclave at 85–90°.

*Glutathione*.—B. Hegedus<sup>130</sup> has published a synthesis of glutathione ( $\gamma$ -glutamyl-cysteinyl-glycine). This synthesis is divided into three stages; in the first stage S-benzyl-L-cystein was esterified and carboxybenzoxylated, then treated with hydrazinehydrate, yielding S-benzyl-N-carboxybenzoxyl-L-cysteinyl-hydrazide (72% overall from benzyl-cystein). With nitrous acid this gave the acid azide, which was then coupled with ethyl aminoacetate; the product was saponified and then rebenzylated to S-benzyl-L-cysteinylglycine.

In the second stage the ethyl ester of L-glutamic acid was carboxybenzoxylated and then converted to the hydrazide. In the third and final stage this hydrazide was treated with nitrous acid and the resulting azide coupled with the methyl ester of the product from stage 1. The resulting compound was treated with dilute sodium hydroxide and then freed from the attached benzyl and carboxybenzoxyl groups by sodium in liquid ammonia. The product, after purification was found identical with the natural substance.

## Steroids

During 1948 it would appear that there has been somewhat of a lessening of what might be described as the continuous battle to secure valuable products from the few natural steroid sources readily accessible. No doubt this is due to the fact that the stored-up research results from the war years have now been largely published. Two positive trends apparent

to the observer are first of all the notable renewal of interest in some of the cardio-active steroids which have been a little neglected of late and secondly, the surprisingly large number of groups which have commenced serious and systematic work on the complete synthesis of the steroid structure from simple starting materials. Such work has been in progress for many years; it was not unknown to hear rumours of research teams which considered an oestrone synthesis "just round the corner" at a time when the structure of the ovarian hormones was still not perfectly defined. Much valuable and probably disappointing work was carried out before Bachmann published his first undoubted synthesis of one of the natural oestrogens—equilenin—in 1940, and there is much more to be done if the steroid hormones and other pharmacologically important steroids are to be synthesised easily and cheaply from readily obtainable starting materials.

Since the interest in the synthetic oestrogens shows no sign of abating, the oestrogens of the near-steroid type are relegated to the separate section on oestrogens.

*Pregnane derivatives.*—An important paper from the CIBA laboratories, by Ch. Meystre, E. T. Schopp, and A. Wettstein,<sup>131</sup> describes 11-dehydropregesterone as the most active of the progestational hormones, having a potency in rabbits three times that of progesterone. Reference is made to a new, and in the opinion of the reviewer desirable, new term to replace the always awkward expression "progestational hormone"; K. Miescher<sup>132</sup> gives the general term "Sexogen," with three subdivisions oestrogen, androgen, and "Gestogen" for the three types of sex hormone or hormone-like substances. Meystre *et al.* give details of the gestogenic activity of several of the steroids already known to possess this type of activity. 11-Dehydropregesterone was made by collidine treatment of the *p*-toluenesulphonate of 12- $\alpha$ -hydroxyprogesterone.

Pl. A. Plattner, H. Heusser, and A. Segre<sup>133</sup> have published a synthesis of 14-*allo*-17-isopregesterone from 3- $\beta$ -acetoxyaetiochola-5:16-dienic acid nitrile; addition of bromine to one double bond enables the use of N-bromosuccinimide in the usual manner to brominate in the allyl position to the second double bond. Removal of the 5:6-bromine atoms is carried out by the use of alcoholic alkali iodide leaving possible the removal of HBr by pyridine to produce the required third double bond. The resulting 3- $\beta$ -acetoxy-aetiochola-5:14:16-trienic acid nitrile is then converted to the methyl ketone by a Grignard reaction (with hydrolysis of the acetyl group), the product partly hydrogenated to saturate ring D, and oxidised by Oppenauer's method to 14-*allo*-17-isopregesterone.

A. L. Wilds and C. H. Shunk<sup>134</sup> have described the preparation of desoxycorticosterone acetate from 3-keto-aetiochol-4-enic acid having as the essential part a new and improved procedure for preparing the acid chloride of the keto acid by reaction of the sodium salt of the acid with oxalyl chloride. The overall yield obtained is claimed to be higher than any previously reported.

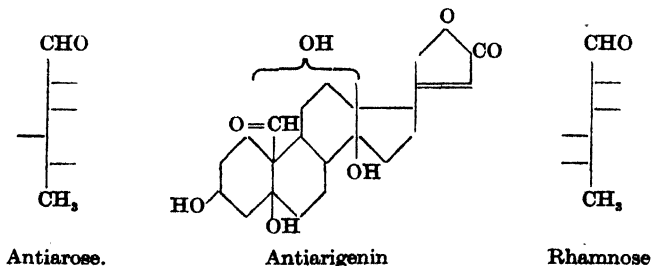
P. L. Julian, E. W. Meyer, and H. C. Printy<sup>135</sup> have published the results of an investigation into the production of pregn-20-enes from

bisnor-steroid acids. They have found that ozonisation of 2-keto-4:20-pregnadiene affords the best route to 3-keto-4-aetiocolenic acid and that hydroxylation of 3-keto-4:20-pregnadiene gave the isomeric 20:21-diols, which they have separated and characterised.

L. H. Sarett<sup>136</sup> has described a new method for the preparation of 17-( $\alpha$ )-hydroxy-20-ketopregnanes. A 20-ketopregnane is converted into its cyanhydrin and dehydrated; the unsaturated nitrile with osmium tetroxide, followed by alkali sulphite yield the 17-( $\alpha$ )-hydroxy-20-ketopregnane. This has been carried out on a 20-keto-21-acetoxypregnane, making possible the synthesis of Kendall's "Compound E." The method is generally desirable as making unnecessary degradation of the C<sub>17</sub> side chain and building-up again in order to obtain the 17-hydroxy-20-keto disposition of groups.

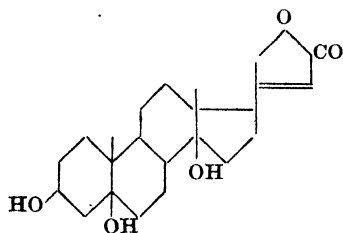
*Cardio-active steroids.*—Attention is drawn to a useful review on the structure and synthesis of the cardiac genins by R. B. Turner of Harvard University.<sup>137</sup> This affords a valuable summary of the state of affairs before this last year's work threw a considerable amount of light on some outstanding problems.

*Antiarins.*—The two antiarins ( $\alpha$  and  $\beta$ ) from *Antiaris toxicaria* Lesch. have remained with structures undecided for many years in spite of considerable work on the subject. These glycosides are among the latest to be taken up by Reichstein and his collaborators in the pharmaceutical establishment of the University of Basel. K. Doebel, E. Schlittler and T. Reichstein<sup>138</sup> have described the isolation and purification of  $\alpha$ -antiarin; repeating past work they have hydrolysed the glycoside to di-anhydro-antiarigenin (also obtainable from the  $\beta$ -glycoside) together with antiarose (the  $\beta$ -glycoside yields L-rhamnose).  $\alpha$ -Antiarin has been reduced to the equally active dihydro- $\alpha$ -antiarin without loss of biological activity, apparently by conversion of the C<sub>10</sub> aldehyde group to the carbinol. The structure is now given with reasonable definition apart from the unknown disposition of one hydroxyl group. This hydroxyl group, since it lactonises with the carboxyl group resulting from the oxidation of the aldehyde group at C<sub>10</sub>, should have the  $\beta$ -configuration; of the positions 7, 11, or 12, the 11  $\beta$  position is considered unlikely. Antiarose is D-gulomethyllose, differing from rhamnose only in the orientation on the carbon atom next to the methyl group.

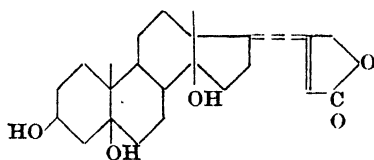


*Periplogenin.*—P. Speiser and T. Reichstein<sup>139</sup> have studied the configuration of periplogenin and alloperiplogenin. The two genins have been degraded by ozonisation of the butenolide rings to the hydroxymethyl

ketones and these oxidised to the carboxylic acids by periodic acid. Two isomeric acids were obtained and these were orientated by the fact that whereas the same oxidation could be effected by chromic acid in the case of *alloperiplogenin*, the intermediate ketoacid was stabilised by lactonising with the hydroxyl group at C<sub>14</sub> in the case of *periplogenin*. The lactone was then converted by alkali to the free keto acid and oxidised by hydrogen peroxide to the same acid obtainable direct from the hydroxymethylketone from *alloperiplogenin*.



Periplogenin.

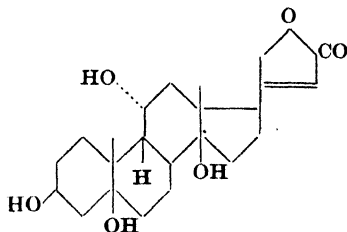
*allo*Periplogenin.

*Strophanthus glycosides*.—The glycosides from the seeds of *Strophanthus nicholsonii* Holm. form the subject of an investigation by J. von Euw and T. Reichstein<sup>140</sup>; 200 grams of seed from the 1947 harvest yielded 143 mg. periplocymarin, 299 mg. cymarin, 180 mg. cymarol, and 690 mg. emicymarin. The first and fourth of these are respectively, the cymaroside and digitaloside of periplogenin, the second the cymaroside of strophanthidin and the third is the C<sub>10</sub> primary alcohol derived from cymarin.

F. Santavy and T. Reichstein<sup>141</sup> have described a new cardio-active glycoside, isolated by them from the seeds of *Euonymus europaea* L. From the German spelling "Evonymus" they have named the new glycoside "Evonoside"; it is presumably correct to use the English form Euonoside. Euonoside and its acetate have been progressively broken down by strophanthobiase yielding in the first stage euobioside and D-glucose; further treatment with the enzyme produced a second molecule of D-glucose and euomonoside which is the rhamnoside of a digitaloid type genin.

A. Buzas and T. Reichstein,<sup>142</sup> in the course of some work on Hellebrin (from *Helleborus niger* L.), have oxidised the triacetate of desglucohellebrin to the triacetyl carboxylic acid.

A. Katz<sup>143</sup> has published the results of an investigation into the constitution of sarmentogenin, the aglycone derived from sarmentocymarin (*Strophanthus sarmentosus*). The diacetate, which exhibits the expected ultra-violet absorption for an unsaturated lactone of the digitalis/strophanthus type, was oxidised by permanganate to a carboxylic acid in which the unacetylated hydroxyl group of the diacetate remained unaffected. Dehydration and hydrogenation of the unsaturated acid yielded an acid whose methyl ester was found identical with 3 $\beta$ :11 $\alpha$ -diacetoxyaetiocholanolic methyl ester. The structure of sarmentogenin may accordingly be regarded as established.



Sarmetogenin.

*Thevetin*.—The glycoside of *Thevetia neriifolia* Juss. has been studied by H. Helfenberger and T. Reichstein.<sup>144</sup> Useful details are given in this paper for the isolation of thevetin from the seeds. The enzyme strophanthobiase has been used to split off the two more readily removable sugar residues (both D-glucose) and a new monoglycoside, neriifolin, obtained; this substance has been found to be five times as toxic as thevetin. Neriifolin could not be split by hydrogen chloride in acetone to give the true aglycone, but a small quantity of anhydro-digitoxigenin was obtained; it is probably, therefore, that neriifolin and thevetin are glycosides of digitoxigenin rather than of its C<sub>3</sub> epimer as was formerly believed.

A group of American workers<sup>145</sup> have investigated the cardiotonic properties of thevetin and find it to be most promising as a drug for use in the treatment of acute heart failure with pulmonary oedema; it has the advantage of very rapid action on intravenous injection coupled with very rapid elimination.

*Degradative oxidation of sterols*.—Two papers (Nos. 3 and 4 of a series) by Miescher and his collaborators have dealt with the by-products of the chromic acid oxidation of cholesterol acetate. The acid fraction left after removal of the known constituents 3 $\beta$ -hydroxy-cholesterol-5-enoic acid and 3 $\beta$ -hydroxycholesterol-5-enoic acid has yielded 3 $\beta$ -hydroxybisanthrochol-5-enoic acid (water-insoluble sodium salt fraction) and 3 $\beta$ -hydroxybisanthrochol-5-enoic acid (water-soluble sodium salt fraction).<sup>146</sup>

The residues from the crystallisation of dehydroisoandrosterone acetate semicarbazone have yielded androsta-3:5-diene-7:17-dione,<sup>147</sup> though it would appear that the actual material present in the semicarbazone residues is 3 $\beta$ -acetoxyandrost-5-ene-7:17-dione, losing water after hydrolysis of the acetoxy group as a result of rather drastic treatment with hydrochloric acid.

E. B. Hershberg<sup>148</sup> has described a new and very useful method for regeneration of acetoxy steroid ketones from their semicarbazones. 50% aqueous pyruvic acid in acetic acid, buffered with sodium acetate, is used as the hydrolysing agent. Pure dehydroisoandrosterone acetate semicarbazone gave a 97.2% yield of dehydroisoandrosterone acetate (m.p. 170.2–170.9). Without sodium acetate there was found to be appreciable hydrolysis of the acetoxy group.

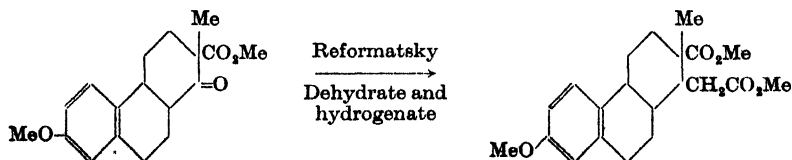
*Synthetic approach to the steroid structure*.—J. A. Hogg<sup>149</sup> of the Upjohn Company research laboratories has made good use of Hagemann's ester (3-methyl-4-carbethoxy-cyclohex-2-ene-1-one), which had been shown

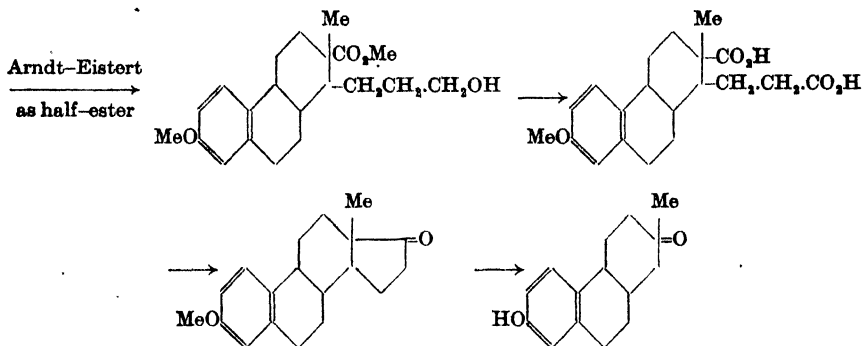
previously to alkylate in the 2-position. He has alkylated the ester with *m*-methoxyphenylethyl bromide and cyclised the product both before and after hydrogenation of the ethylenic bond. The two cyclised products, 1-methyl-2-carboxy-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene and the corresponding 3 : 4 : 9 : 10-tetrahydrophenanthrene were both selenium dehydrogenated to the known 1-methyl-7-methoxyphenanthrene. An angular methyl group was introduced by direct alkylation of the hexahydrophenanthrene; two products were obtained, of which the principal constituent considered to be the *trans* isomer was found to have an oestrogenic activity approximately four times that of oestrone. These experiments are regarded by the author as models for further work, to be directed towards the use of this approach to the full steroid structure.

A. L. Wilds and T. L. Johnson<sup>150</sup> (University of Wisconsin) have reported a 20-step total synthesis of an isomer of oestrone having the keto group at C<sub>16</sub>. Very low oestrogenic activity indicated that this isomer also differed from oestrone stereochemically. The key intermediate in this synthesis was the 1-keto-2-methyl-7-methoxy-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-octhydrophenanthrene for which an improved method of preparation had previously been published by Bachmann, Kushner, and Stevenson<sup>151</sup>; the present authors claim further improvement in the yield. The ketone was alkylated apparently in the desired position, with methyl bromoacetate, the resulting acid converted to the methyl ketone and the ketone cyclised with sodium methoxide. The methoxy unsaturated ketone was then hydrogenated and demethylated to the required oestrone isomer.

W. E. Bachmann and L. B. Scott<sup>152</sup> have studied the reaction of 1-vinylnaphthalene and of 6-methoxy-1-vinylnaphthalene with citraconic anhydride, fumaric acid, and mesaconic acid. This work has been extended by W. E. Bachmann and J. M. Chemerda,<sup>153</sup> who have carried out the Diels-Alder reaction of 1-vinyl-6-methoxy-3 : 4-dihydronaphthalene with citraconic anhydride. Two structurally isomeric adducts were obtained; one was identified as *cis*-1-methyl-7-methoxy-hexahydrophenanthrene-1 : 2-dicarboxylic acid anhydride and the other as the 2-methyl isomer. The 1-methyl-hexahydro acid was hydrogenated to the octahydro acid, two Arndt-Eistert reactions carried out on the half-ester and the lead salt of the final acid pyrolysed, giving a neutral product believed to be the methyl ether of an isomer of oestrone. Further work on the 2-methylhexahydro acid is hoped to result in the production of oestrone or its stereoisomers.

G. Anner and K. Miescher<sup>154</sup> have described a total synthesis of natural oestrone; the essential final stages are most readily followed from the structural diagram below :





The resulting racemic oestrone was separated into the two forms by the use of the (—)-menthoxyacetyl derivatives. Upon hydrolysis the (+)-oestrone was found to be indistinguishable from natural oestrone. The dehydrated and hydrogenated Reformatsky ester in the above account was obtained in two forms, the higher melting variety being employed for the completion of the oestrone synthesis. The lower melting form was also submitted to the same procedure with the ultimate production of a racemic oestrone not identical with the natural.

J. Heer and K. Miescher<sup>155</sup> have used the same approach to prepare a monodehydro-oestrone starting from the half-ester of 7-methyl-monodehydro-marrianolic acid. The final product was dehydrogenated under mild conditions, in the form of the methyl ether, and was found to give *isoequilenin* methyl ether.

J. W. Cook and R. Philip<sup>156</sup> have published the first paper in a new series on synthetic studies in the steroid series. This is concerned with the use of methyl- $\gamma$ -bromocrotonate in the possible syntheses of fully reduced compounds of the steroid series. A new method has been given for the preparation of *cis*-9-methyl-1-decalone, which is regarded as a suitable intermediate for the synthesis of compounds of the *actiocholane* series.

C. A. Grob<sup>157</sup> and his collaborators have published two papers forming the first two parts of a plan of work in this field being carried out in the organic chemistry department of Basel University, while another series has been commenced by E. Buchta<sup>158</sup> and his co-workers at the University of Erlangen.

## Oestrogens

This section is of necessity almost inextricably intertwined with the reports on the synthetic approach to the steroid structure in the previous section. This is inevitable inasmuch as most approaches to oestrone along the lines of total synthesis must pass through the related group of oestrogenic carboxylic acids which Miescher and his collaborators in the CIBA A.-G. research laboratories have made so much their own subject.

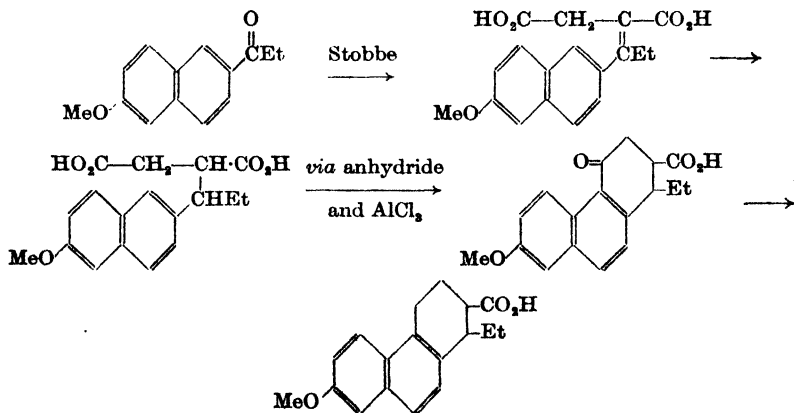
Working on similar lines to Bachmann and Scott,<sup>152</sup> J. Heer and K. Miescher<sup>159</sup> have carried out a reaction between citraconic anhydride

and 1-vinyl-6-methoxy-3:4-dihydronaphthalene, obtaining and orientating both isomeric 1(or 2)-methyl-7-methoxy-1:2:3:9:10:11-hexahydrophenanthrene-1:2-dicarboxylic acids from the originally formed anhydrides. Both acids have been isomerised to the corresponding 1:2:3:4:9:10-hexahydro acids.

These same authors<sup>160</sup> have converted equilenin methyl ether into (+)- $\beta$ -7-methylbisdehydrodoisynolic acid under sufficiently mild conditions to be able to conclude that the two have the same steric (*trans*) configuration. This paper is one of several from this research team, which is making a very notable attempt to clear up the problems of steric relationships throughout the steroid field. Another important contribution to this subject from the same source has been published under the names of J. R. Billeter and K. Miescher.<sup>161</sup>

J. Heer and K. Miescher<sup>162</sup> have continued with the work commenced under the reference above<sup>159</sup>; the dimethyl esters of the two 2-methyl-7-methoxyhexahydrophenanthrene-1:2-dicarboxylic acids have been converted to their half-esters by gentle hydrolysis and the acid chlorides submitted to the Arndt-Eistert reaction; this procedure yields the homologous acids in which the chain-lengthening has taken place in the carbon chain on C<sub>2</sub>. By treatment of the acid anhydrides with sodium methoxide the alternative half-esters are obtained, from which homologous acids can again be built up.

W. S. Johnson and W. P. Graber<sup>163</sup> have announced a new synthesis of one of the most important of the group of oestrogenic carboxylic acids—*bis*-dehydrodoisynolic acid. Previous preparations of this acid have been carried out by Heer, Billeter, and Miescher,<sup>164</sup> and by Anner and Miescher.<sup>165</sup> The new synthesis is depicted below:



Hydrogenation of the keto acid was carried out by using a palladium-on-charcoal catalyst in the presence of perchloric acid; the angular methyl group was introduced in the last stage by treating the methyl ether with methyl iodide in the presence of sodium triphenylmethyl. The resulting methyl ether appeared to be identical with a specimen of authentic *bis*-dehydrodoisynolic ester methyl ether and the biological activity of the acid was of the right order.

*Stilboestrol group*.—J. A. Hunter and J. Korman<sup>166</sup> have prepared an oestrogen which combines the structural types of doisyolic acid and of "hexoestrol"; this is  $\alpha$ -methyl- $\alpha\beta$ -di-(*p*-hydroxyphenyl)-valeric acid, which is essentially "hexoestrol" in which the substituents on one of the central carbon atoms (H and ethyl) are replaced by methyl and carboxyl. Preliminary results indicate that this acid produces full oestrous response in doses of 20  $\mu$ g. in castrated rats.

V. Niederl, C. A. Siconolfi, A. Bloom, and C. T. van Meter,<sup>167</sup> have made homologues of both "hexoestrol" and "dienoestrol" in which the phenyl groups bear methyl groups in the *meta* position and have also made a large number of esters of these two substances. 3 : 4-*bis*-(*m*-methyl-*p*-hydroxyphenyl)-2 : 4-hexadiene was found to give a full response in doses of 5  $\mu$ g. in castrated rats, by injection, while the corresponding hexane was found approximately three times as active. Toxicities were found to be quite low and it is hoped that the substances, together with some of their more interesting esters, may prove useful in clinical tests.

This work has been extended by J. B. Niederl and R. M. Silverstein<sup>168</sup> to the preparation and study of phenyl and benzyl groups attached in the *meta* position, to the molecules of "hexoestrol" and "dienoestrol." The effect of these groups was greatly to decrease the oestrogenic activity. J. B. Niederl and P. Weiss<sup>169</sup> have further extended this line of research by building up tetra-alkyl substituted "hexoestrols" and "dienoestrols" from the three phenols *p*-xylenol, thymol, and carvacrol. The phenols were esterified with propionyl chloride and subjected to the Fries rearrangement; the resulting 2 : 5-dialkyl-4-hydroxypropiophenones were then reduced to the pinacols, dehydrated to the dienes and hydrogenated to the hexanes. Only the products from *p*-xylenol were found to be potent oestrogens, the tetramethylhexoestrol comparing favourably with the dimethyl derivative (above).

M. J. Freiman<sup>170</sup> has prepared a member of the "stilboestrol" series having three conjugated double bonds in the *n*-hexane chain. This substance was made by reaction of N-bromosuccinimide with the dipropionate of (diethyl)"stilboestrol" followed by elimination of 2 mols. of hydrogen bromide from the dibromo derivative.

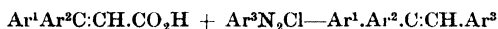
Huang-Minlon,<sup>171</sup> in the course of work on the reaction of hydrazine hydrate with nitro compounds, has found a novel route to "hexoestrol" and "isohexoestrol." *p*-Nitropropylbenzene on heating with hydrazine hydrate and alkali gives both *meso* and racemic 4 : 4'-diamino-diphenylhexane, in addition to *p*-aminopropylbenzene. Both diamino compounds were converted to the phenols by diazotisation, followed by heating with water. The yields of diamine were of the order of 10%.

K. Sisido and H. Nozaki<sup>172</sup> have published the first two papers of a series on the preparation of synthetic oestrogens. The first of these is concerned with the synthesis of (diethyl)"stilboestrol" through the pinacol-pinacolone compounds and is based on the work of Wessely, Kerschbaum, Kleedorfer, Prillinger, and Zajic<sup>173</sup> on the use of the pinacol-pinacolone and retropinacolone rearrangements. *p*-Methoxypropiophenone was reduced to the pinacol in the usual manner, the pinacol treated with sulphuric acid to produce the pinacolone, which was then

reduced with sodium to the carbinol and submitted to the retropinacolone rearrangement, yielding the dimethyl ether of "stilboestrol."

The second paper deals with the preparation of "hexoestrol" from anethole hydrochloride or hydrobromide in 10 or 15% yield by de-halogenating with iron powder in the presence of water, followed by a usual type de-methylation. This method is of interest, particularly since anhydrous conditions are not used for the de-halogenation; the authors refer to the statement of Quelet<sup>174</sup> to the effect that  $\alpha$ -halogenoalkyl-anisoles are more stable in the presence of water.

*Triarylethylenes.*—F. Bergmann, E. Dimant, and H. Japhe<sup>175</sup> have published a new synthesis of triarylethylenes; they have coupled 2:2-diarylacrylic acids with diazotised aromatic primary amines, a reaction analogous to the Meerwein synthesis of stilbenes from cinnamic acids.



P. R. Carter and D. H. Hey<sup>176</sup> have prepared a series of new mono-, di-, and tri-*p*-alkoxytriphenylbromoethylenes, by bromination of the corresponding diphenylbenzyl carbinols.

### Miscellaneous

*bis-Trimethylammonium compounds with curare-like activity.*—The curare-like action of polymethylene bisquaternary salts is the subject of some important announcements made by R. B. Barlow and H. R. Ing,<sup>177</sup> of the Department of Pharmacology, Oxford, and by W. D. M. Paton and E. J. Zaimis,<sup>178</sup> of the National Institute for Medical Research. The former authors have approached the subject from the consideration of the general shape of the molecule of tubocurarine; they have prepared and studied a series of polymethylene *bis*-trimethyl and *bis*-triethyl ammonium bromides with chain lengths of 2–5 and 7–13 carbon atoms. In the rabbit head-drop test, in the *bis*-trimethyl ammonium bromide series activity rose to a maximum in the C<sub>10</sub> member and then slowly fell with further increase in the chain length. The C<sub>10</sub> member was found to be approximately three times as potent as (+)-tubocurarine chloride.

The latter authors made their first observation of the power of octamethylene- $\alpha$ : $\omega$ -*bis*trimethyl ammonium chloride as a cause of neuro-muscular block, while examining the material in connection with other work. Following on this, they have prepared and examined a series of iodides, finding increase in potency on passing up the series from the ethylene compound to octamethylene, with the decamethylene compound more active still. Using the rabbit head-drop test they also found the C<sub>10</sub> member of the series approximately three times as active as (+)-tubocurarine.

Paton and Zaimis have followed up this first report with a second announcement,<sup>179</sup> in which it is stated that the C<sub>10</sub> *bis*-trimethyl ammonium iodide possesses neuro-muscular blocking activity which may be suitable for clinical use, while the C<sub>6</sub> member may be similarly of value for producing ganglionic block. They draw attention to the important fact that the C<sub>10</sub> compound has much less tendency than (+)-tubocurarine chloride to produce respiratory difficulties and has less power of producing histamine

The C<sub>6</sub> member of the series is also of great importance as an antagonist

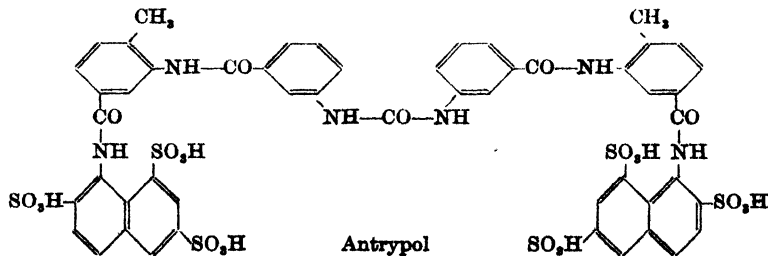
to the  $C_{10}$  compound; eserine and prostigmine do not antagonise and without an effective antagonist the clinical use of the new compound would be fraught with considerable danger.

**Chemotherapy of cholera.**—A notable advance has been made in this subject by the publication by S. S. Bhatnagar, F. Fernandes, J. de Sa and P. V. Divekar<sup>180</sup> of their results obtained in the testing of a CIBA product then known as "6257" but latterly given the name of Formo-Cibazol, in human cholera infection. This substance is a condensation product, of unknown structure, from two molecules of sulphathiazole ("cibazol") with three molecules of formaldehyde. Very low toxicity, probably as a result of low absorption from the intestinal tract, coupled with high specific activity against vibrio-cholerae make this substance a drug of considerable promise.

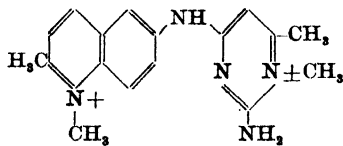
**Chemotherapy of bilharzia.**—One of the drugs discovered as a result of work carried out in the research laboratories of I.G. Farbenindustrie, Elberfeld, during, or just prior to the late war, was Miracil D. According to a C.I.O.S.<sup>181</sup> report, Kikuth considered this substance as showing therapeutic activity for mice and monkeys infected with *bilharzia* (*schistosoma*) *mansoni*. A preliminary communication from M. A. Azim, A. Halawani, and J. M. Watson<sup>182</sup> has given the results of laboratory experiments and clinical trials of the drug. While the findings are not so satisfactory as could be desired, these authors have been able to state that "Miracil D is the first drug given by mouth which has shown significant activity in the treatment of this disease, and it may prove to be the forerunner of others which will kill the parasites in man, quickly, surely, and safely."

Miracil D is one of a short series of miracils, which are the subject of a paper by H. Mauss<sup>183</sup> describing the preparation of all of them. The miracils are all related to 1-methyl-4-(diethylaminoethylamino)-xanthone, of which A is the hydrochloride, B is the 7-chloro derivative, C is the corresponding carbinol, and D is the corresponding hydrochloride of the thioxanthone. Full manufacturing details for the preparation of miracil D were given in a C.I.O.S. report<sup>184</sup> and also in a B.I.O.S. report.<sup>185</sup>

**Chemotherapy of trypanosomiasis.**—W. Smith and W. G. Reid,<sup>186</sup> in the course of an account of the development of the manufacture of pharmaceutical products by I.C.I., include the route to the trypanocide antrypol, used in human sleeping sickness.  $\alpha$ -naphthylamine-2:6:8-trisulphonic acid is condensed with *o*-nitro-*p*-toluyl chloride, the product reduced (nitro to amino), and the product brought into reaction with *m*-nitrobenzoyl chloride. The amine resulting from a second reduction is then converted to the substituted carbamide.



Great interest has been shown in the announcement towards the end of the year by I.C.I. of the preparation and very promising field tests of a new trypanocidal drug, "Antrycide." Antrycide is a 4-amino-6-(2'-amino-6'-methylpyrimidyl-4'-amino) quinaldine-1 : 1'-dimetho salt derived from a variety of acids. Veterinary trials in Africa have been commenced and have shown very promising results. Antrycide salts, administered easily and safely in single doses, have cured infections of *T. congolense*, *T. vivax*, and *T. brucei* in cattle, *T. brucei* in horses, donkeys and dogs and *T. evansi* in camels. Considerable protection has been afforded to cattle against subsequent infection with *T. congolense* and *T. vivax*. The announcement has been made by F. H. S. Curd and D. G. Davey<sup>187</sup> early in 1949.



Antrycide

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# ANTIBIOTICS

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THE publication for the first time of a report concerned solely with antibiotics is symptomatic of the important position now occupied by this branch of medicinal chemistry. The amounts of penicillin and streptomycin produced in the United States and the United Kingdom have, indeed, shown phenomenal increases in recent years. Thus, the amounts of penicillin produced in the two countries in 1944 were 1,600,000 and 36,000 mega-units respectively, whilst the corresponding amounts for 1947 were 41,400,000 and 4,900,000 mega-units, and for the first 10 months of 1948, 76,600,000 and 7,300,000 mega-units. In the United States, the production of streptomycin, which began in 1945, amounted in 1947 to 9687 kg. and in the first 10 months of 1948 to 27,000 kg. In 1946, the sales values of the two antibiotics in the U.S.A. were \$89,600,000 and \$6,000,000 respectively; by contrast, the value of all the sulphonamides produced in the same period was \$23,300,000. At the same time, the hospital price of penicillin fell from \$2.40-2.60 per 100,000 units on 1st January 1945 to 38 cents at the beginning of 1947.

## Penicillin

*Legislation.*—Penicillin was brought within the scope of the Therapeutic Substances Act 1925 by Regulations made in 1944. These have since then been amended, and Regulations made in 1947 extended the Act to preparations of penicillin for parenteral administration. Penicillin and its preparations intended for use in this way must satisfy the requirements of the Therapeutic Substances Amendment Regulations 1946 (S.R.O. 1946, No. 467) as amended by the Regulations of 1948 (S.I. 1948, No. 2418); they must pass approved tests for potency (in the case of penicillin in solid form, this must not be less than 900 units per mg.), toxicity, and pyrogens. The labels on the containers must also conform with certain requirements.

The Penicillin Act 1947 was passed in order to minimise the possible public health hazards resulting from widespread self-medication with penicillin preparations. This Act restricts the sale or supply of penicillin to medical or dental practitioners, veterinary surgeons or persons acting under their directions or to pharmacists or authorised sellers of poisons under a prescription from a practitioner or surgeon. It also prohibits the administration of penicillin except by a practitioner or by someone acting on his instructions. The Act empowers the Minister to make regulations extending the Act to other antibiotics, but up to the present no such regulations have been made.

*Penicillin fermentation.*—The surface-culture method, adopted by Sir Howard Florey and his colleagues in their original work, is no longer used for the commercial production of penicillin. The "deep-culture"

or "submerged-culture" method<sup>1</sup> is now standard practice, the mould being grown on a suitable medium in large tanks (up to 10,000 gallons capacity) using up to 1 volume of sterile air per volume of liquor per minute for aeration and agitation; in some factories, the liquor is stirred mechanically as well. The culture medium originally used consisted of a solution of lactose and corn steep liquor, and it was inoculated with a strain (No. 832) of *Penicillium chrysogenum*. Considerably better yields were obtained with new strains of the mould derived from No. 832 by irradiation with X-rays, giving strain X1612, and then irradiating X1612 with ultra-violet light, producing thereby Q176. This is believed to be the strain at present in use throughout the world, although slight improvements may have been effected by a process of selection. Fermentation with the X-ray mutant has been patented in the U.S.A., the patent being dedicated to the American public.<sup>2</sup>

During the past 12 months or so, several patents have been published claiming improved media for penicillin production, for example, a medium containing proteinaceous material such as corn steep liquor, soya bean meal, cottonseed meal, yeast extract, wheat germ, whisky slop or *Penicillium* autolysate, together with glycerol or a carbohydrate such as brown sugar, starch, dextrose, molasses or sucrose, and mineral salts.<sup>3</sup> Improvements are said to result from the addition of 0.02 to 0.65% of sulphite,<sup>4</sup> and from treatment of the medium with chlorine dioxide diluted with an inert gas.<sup>5</sup>

The most recent developments in penicillin fermentation have arisen from the use of precursors. R. D. Coghill and A. J. Moyer<sup>6</sup> found that improved yields of penicillin were obtained following the addition to the medium of 0.005 to 0.5 g. of phenylacetic acid per 100 ml., whilst E. Lester Smith and A. E. Bide<sup>7</sup> independently made the same discovery, and showed in addition that phenylacetamide and certain other derivatives of phenylacetic acid were effective. T. H. Mead and M. V. Slack<sup>8</sup> isolated  $\beta$ -phenylethylamine from corn steep liquor and showed that it also acted as a precursor of benzylpenicillin (penicillin G), suggesting one possible rôle of corn steep liquor in the penicillin fermentation. *p*-Hydroxy-phenylethylamine was also isolated from corn steep liquor and shown to be a precursor of hydroxybenzyl penicillin (penicillin X). Corn steep liquor has other functions besides supplying precursors, since it gives increased yields when added to a medium already containing optimal amounts of precursor. In spite of its disadvantages, therefore, corn steep liquor continues to be used in penicillin production. Attempts have been made to remove inert materials from it, for example, by neutralising with alkali, with or without a prior yeast fermentation.<sup>9</sup>

A large number of substances derived from phenylacetic acid have been tested as precursors of benzylpenicillin, and several have been claimed to be superior to the parent substance.<sup>10</sup> It is doubtful, however, whether any of these more complicated substances have any advantages over phenylacetic acid, as they are probably converted into the acid or a simple derivative before incorporation into the penicillin molecule. Certainly they are more expensive to make than phenylacetic acid.

The biochemistry of the penicillin fermentation is by no means fully understood, but F. G. Jarvis and M. J. Johnson<sup>11</sup> have added considerably

to our knowledge. They showed that the process comprises two phases, a growth phase in which little penicillin formation occurs and a penicillin production phase in which little or no growth takes place. The optimal  $p_H$  for growth was 6.8 and for penicillin production 7.3. They devised a synthetic medium, containing lactose, glucose, ammonia, acetate, lactate, and inorganic salts, that satisfied the  $p_H$  requirements for both phases of the fermentation and gave a yield of 300 units per ml. When supplemented with  $\beta$ -phenylethylamine acetate, this increased to 500 units per ml. With a corn steep liquor medium, however, a still higher yield of 700 units per ml. was obtained, again demonstrating the presence in corn steep liquor of other substances favouring penicillin production. The amino acid metabolism of *P. chrysogenum* was studied by F. T. Wolf,<sup>12</sup> who found that alanine, glutamic acid, and proline were oxidised rapidly, and the other amino acids much more slowly. Corn steep liquor contains a high proportion of both alanine and glutamic acid.<sup>13</sup>

Previous attempts to establish the origin of the sulphur atom in penicillin indicates that it was probably derived from inorganic sulphate ions. This has recently been confirmed<sup>14</sup> by growing the mould on a medium containing sodium sulphate with a radio-active sulphur atom and subsequently isolating benzylpenicillin with radio-active sulphur in the molecule.

*Isolation and purification.*—The method of recovering penicillin from fermentation liquors by adsorption on carbon and elution of the adsorbate is now obsolete, having been superseded by direct extraction of the acidified liquor with a solvent such as butyl or amyl acetate. One of the chief difficulties encountered in this process is emulsification, which is avoided by adding a surface-active agent to the broth prior to extraction. The use of emulsifying agents, such as sulphated or sulphonated alcohols, the condensation product of formaldehyde and naphthalene sulphonic acid or the sodium sulphate derivative of 3:9-diethyltridecanol-6, in amounts sufficient to hasten demulsification has been patented.<sup>15</sup> Another patent<sup>16</sup> covers the use for the same purpose of an oxazoline containing a hydroxymethyl group and a long alkyl chain, *e.g.*, the compound made by allowing 2-amino-2-methyl-1:3-propanediol to react with coconut oil fatty acids.

It is obvious that the extraction of fermentation liquors of low  $p_H$  with organic solvents will remove other organic acids besides penicillin and that these will contaminate the penicillin salt prepared from such extracts by extraction with alkali. Some of these impurities are said to be eliminated by washing the solvent extract with water,<sup>17</sup> but a much greater degree of purification is obtained if the crude material is partitioned between water, or better a buffer solution, and a solvent flowing counter-current to it, and an acid stronger than penicillin is introduced at a point between the points of entry of the two phases.<sup>18</sup> In this way a  $p_H$  gradient is established from the top to the bottom of the column. The separated solvent extract phase is washed with water and the washings returned to the column together with fresh aqueous solution. Up to 60% of the acids weaker than penicillin can be eliminated by this method, the best results being obtained by injecting the stripping acid near the solvent inlet.

Many other methods of purifying crude penicillin have been described. Thus an aqueous solution of  $p_R$  2.5-3.0 may be extracted with an aliphatic hydrocarbon, penicillin then recovered from the aqueous solution by extraction with one of the usual solvents, and pigment removed from the solvent extract by an adsorbent such as magnesium ammonium phosphate or "aged" urea.<sup>19</sup> Chromatography of an aqueous solution of an alkaline earth salt of penicillin on a column of alumina has also been used with or without an auxiliary column of magnesium silicate.<sup>20</sup> Impurities are said to be removed by adding to the aqueous solution a diazotised arylamine, which couples with impurities to form coloured azo compounds.<sup>21</sup>

The most important development in the purification of penicillin during 1948, however, was the introduction of crystalline salts of penicillin. Amorphous sodium penicillin is not easy to crystallise unless it is relatively pure, and the requisite degree of purity was originally attained by combining penicillin with certain organic bases. The salts thus formed crystallised and were then converted back to the sodium or other metallic salts. This process is of commercial importance and amongst the organic bases used for this purpose are N-ethylpiperidine, N-methyl piperidine, N-ethyl morpholine,<sup>22</sup> cyclohexylamine, and methyl cyclohexylamine.<sup>23</sup>

Although the replacement of amorphous sodium penicillin by the crystalline salt eliminates the expensive freeze-drying process, it introduces additional complications in that the final crystallisation has to be carried out under sterile conditions. The product is, however, free from toxic impurities and it is far more stable than the amorphous salt, with a shelf-life of three years compared with only about a year. It should be noted, however, that solutions of crystalline sodium penicillin may be actually less stable than those of the amorphous salt because buffering substances have been removed from it. Crystalline sodium penicillin can be prepared from the amorphous salt, purified as above, by crystallisation from an aliphatic alcohol containing not more than six carbon atoms.<sup>24</sup>

*Assay.*—The cup plate method, or its many modifications, of assaying penicillin, continue to be used as the standard method of assessing the potency of commercial penicillin, but one or other of several chemical methods is being increasingly used in research work. At the beginning of 1948, the Society of Public Analysts held a discussion meeting on methods of assay, at which the available methods, both chemical and micro-biological, were reviewed.<sup>25</sup> A particularly difficult problem was created by the necessity for estimating the benzylpenicillin content of a crude mixture of different species of penicillin, when it was realised that this particular form was therapeutically more effective than the others. In one method of assay, N-ethylpiperidine is used to precipitate the benzylpenicillin preferentially,<sup>26</sup> but in fact, small amounts of other penicillins are precipitated at the same time and some of the benzylpenicillin remains in solution; the accuracy of the method thus appears to depend on selecting conditions in which the errors balance one another. Nevertheless, the method has been accepted by the U.S. Food and Drug Administration as official for benzylpenicillin. In another method, benzylpenicillin is preferentially adsorbed on a column of "Super-Filtrol" and eluted as a separate fraction.<sup>27</sup> In this country, and increasingly in

the U.S.A., the partition chromatographic method of R. R. Goodall and A. A. Levi<sup>28</sup> is preferred, as it not only estimates benzylpenicillin with a fair degree of accuracy, but all the other penicillins present as well—including several that have not yet been characterised; it also requires very small amounts of material. Although the equipment required is somewhat elaborate, it can be adapted to the assay of quite a large number of samples per day.

*Presentation.*—Sodium penicillin is rapidly excreted following intravenous injection, so that the concentration in the blood soon falls to a level insufficient to inhibit bacterial growth. Attempts have been made by various means to prolong the therapeutic level. One way in which the problem has been successfully solved is by the oral administration of "Caronamide" (*p*-carboxyphenylmethane sulphonanilide) at the same time as the penicillin is injected. "Caronamide" competes with penicillin (and other substances excreted by this route) for the renal tubular excretory transport mechanism. Although at first sight this may appear to be a physiologically unsound procedure, in practice it is giving good results with no apparent harm to the patient.<sup>29</sup> The first method to be used successfully for producing a prolonged therapeutic blood-level was based on a different principle, namely the injection of a sterile suspension of sodium or calcium penicillin in a mixture of arachis oil and beeswax. The thick oil forms a depot, from which the penicillin is slowly leached out and released into the blood-stream; without the beeswax, the penicillin dissolves out much too quickly. Unfortunately, however, the injection of this very viscous suspension is no easy matter and may give the patient considerable pain. Recently, a suspension of the water-insoluble procaine salt of penicillin in arachis oil has been introduced. This gives a prolonged therapeutic blood level at least equal to that given by the oil-beeswax preparation.<sup>30</sup> Because beeswax is absent, the suspension is much more mobile and therefore easier to inject. Other water-insoluble salts of penicillin have a similar effect to the procaine salt in delaying extraction from the oily depot.

Our knowledge of the way in which penicillin exerts its anti-bacterial effect is still very limited. It has been known since 1941 that striking morphological changes take place in cells grown in presence of a sub-lethal concentration of penicillin; although the cells multiply they do not divide but form long threads. It would seem that penicillin interferes with multiplication by inhibiting cytoplasmic rather than nuclear division.<sup>31</sup> The most important clue so far obtained relating to the problem of penicillin bacteriostasis is provided by E. F. Gale's observation that the drug interferes with glutamic acid metabolism.<sup>32</sup> Normally, when *Staphylococcus aureus* is grown in a medium containing glutamic acid this substance accumulates within the cell in steadily increasing concentrations. On the addition of penicillin, however, the concentration of glutamic acid within the cells rapidly decreases. Assimilation of this amino acid is in fact completely inhibited and protein synthesis, and therefore growth, can no longer take place. Moreover, the assimilation of glutamic acid is related to the penicillin sensitivity of the cell, and the more resistant the cell becomes, the more completely it loses its power to concentrate free glutamic acid in the internal environment. Very

resistant organisms in fact are able to synthesise the amino acids they require from ammonia and glucose, and thus become independent of their external environment. It has been shown<sup>33</sup> that penicillin does not block the passage of glutamic acid through the cell wall by being itself adsorbed. This effect on glutamic acid metabolism may not be the only way in which penicillin acts on bacteria, and inhibitory actions on ribonuclease<sup>34</sup> and on glutathione metabolism<sup>35</sup> have been suggested as possible explanations of its anti-bacterial effect. The presence of cobalt markedly reduced the concentration of penicillin required to inhibit the proliferation of *Staphylococcus aureus* and the addition of small amounts of cobalt to penicillin doubled the effectiveness of the latter against *Eberthella typhosa* in adult mice.<sup>36</sup> The significance of these observations is not yet apparent.

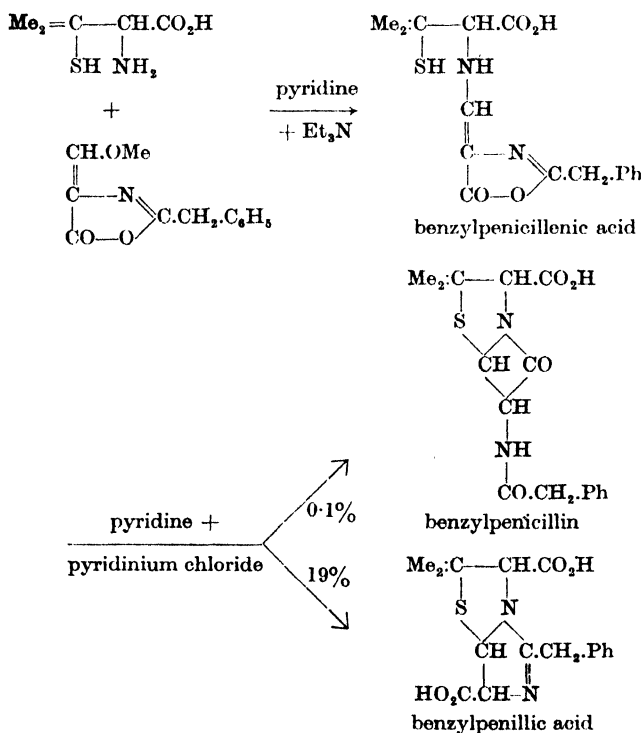
*Chemistry of penicillin.*—In last year's Annual Report, reference was made to a monograph on the Chemistry of Penicillin, which described in detail the work carried out in the U.K. and U.S.A. during the war, on the structure of penicillin and the attempts to synthesise it. Publication of these results was delayed for security reasons under an agreement between the two Governments signed in 1946 (Cmd. 6757). The agreement became effective as from 1st December 1943, and continues in force until the last of the patents involved has expired. It is expected that the monograph will be available in the very near future. In the meantime, useful summaries of the main conclusions resulting from the work have been published by E. Chain<sup>37</sup> and A. H. Cook.<sup>38</sup>

A large number of new compounds were made in the course of this work and many of these are the subject of patent specifications which are only now beginning to be published by the Patent Office because of the delay imposed by the secrecy provisions, already referred to. Although some of these substances were used by V. du Vigneaud and his colleagues in synthesising penicillin, the yields obtained were so low that the method hardly seems of practical importance at the present time and the intermediates used are therefore only of academic interest and do not appear to call for discussion in this review. Should du Vigneaud's method ever be improved so that good yields of penicillin are obtained, then these intermediates will, of course, immediately become of considerable importance.

More information relevant to the chemistry of penicillin has become available since the compilation of the penicillin monograph, and is being published in the scientific journals in the ordinary way. An anhydride of benzylpenicillin has been prepared and treated with  $\beta$ -dimethylamino-ethanol to give the corresponding ester of penicillin,<sup>39</sup> whilst penicillin acetyl anhydride was prepared and treated with a concentrated solution of ammonium phosphate to give penicillin amide.<sup>40</sup> Both these penicillin derivatives have potential value as therapeutic agents, and it has been shown that the amide is unaffected by penicillinase, so that it may be effective against organisms resistant to ordinary penicillin.

V. du Vigneaud and his colleagues have continued their investigations on the mechanism of the reaction by which small amounts of benzylpenicillin have been synthesised, namely that between penicillamine and 2-benzyl-4-methoxymethylene-5(4)-oxazolone. They have shown<sup>41</sup> that,

under certain conditions, this gives a 19% yield of benzylpenillic acid, which can also be prepared in good yield from benzylpenicillenic acid. They showed that the latter was an intermediate in the formation of benzylpenillic acid from benzylpenicillin and that when it is heated in pyridine containing pyridinium chloride antibiotic activity is produced in amounts comparable with that obtained in the penicillamine-oxazolone reaction. Proof was obtained<sup>42</sup> that the antibacterial activity was due to penicillin and not to an impurity by showing that the amount of activity formed by heating ( $\pm$ )-benzylpenicillenic acid containing the natural (+)-isomer with pyridine-pyridinium chloride was the same as that produced by similar treatment of the optically inactive acid containing the synthetic (+)-isomer. We may therefore formulate the important reaction between penicillamine and the oxazolone as:



This reaction has now been used<sup>43</sup> to synthesise new penicillins in very small amounts although sufficient was obtained to enable their biological properties to be compared. The oxazolone mentioned above was condensed with ( $\pm$ )- $\beta$ -methylcysteine, ( $\pm$ )- $\beta\beta$ -diethylcysteine, and ( $\pm$ )- $\beta$ -ethyl- $\beta$ -methylcysteine, whilst (+)-penicillamine was condensed with 2-phenyl- and 2-styryl-ethoxymethylene-5(4)-oxazolone.

The antibacterial activities of the new penicillins relative to different organisms showed wide variations from that exhibited by benzylpenicillin,

but unfortunately none of them inhibited organisms resistant to benzylpenicillin.

A large number of new penicillins have been made by biosynthesis. Interesting though this approach is, the results obtained are strictly limited, for it is only possible to prepare penicillins containing substituents in place of the benzyl group of benzylpenicillin. O. K. Behrens and his colleagues<sup>44</sup> have prepared by this method penicillins derived from arylcarboxylic acids,  $\alpha$ -substituted phenylacetic acids, aliphatic acids, aryl aliphatic (other than acetic) acids, cycloalkyl aliphatic acids and a variety of substituted mercaptoacetic acids. In several instances the new penicillins were formed with virtual exclusion of the "natural" penicillins. The activities of these new penicillins towards micro-organisms differed slightly from one compound to another, but none differed widely from that of benzylpenicillin. The compounds also differed in their relative activities towards benzylpenicillin-resistant strains but, as with du Vigneaud's synthetic compounds, none had a sufficiently marked action to be of therapeutic value.<sup>45</sup>

The penicillin produced by *Aspergillus flavus* has been shown<sup>46</sup> to be *n*-amylpenicillin and not 3-pentenylpenicillin as previously supposed. Its isolation from broth by adsorption on alumina or by extraction of acidified broth with ether has been patented.<sup>47</sup>

## Streptomycin

Streptomycin is the most effective agent yet discovered for the treatment of tuberculosis. Several authoritative reports on its therapeutic value have been published during the year. In this country, the M.R.C. has described the results of treatment with streptomycin in tuberculous meningitis, a disease hitherto invariably fatal.<sup>48</sup> Of 105 cases treated, 30 apparently recovered, the recovery rate being higher in the group in which treatment was given at an early stage of the disease. The M.R.C. has also published a report on the treatment of pulmonary tuberculosis with the drug.<sup>49</sup> It is very difficult to evaluate drugs in the treatment of this condition as it is liable to spontaneous recovery, and this is the first occasion on which a properly controlled trial has been attempted. The selected patients were divided into two approximately equal groups, and both were given exactly the same treatment except that one group received injections of streptomycin and the other injections of a neutral solution. Precautions were taken to prevent any of the staff in charge of the cases from knowing which individuals belonged to the control group and which were receiving streptomycin. The results amply justified this somewhat elaborate method of testing. At the end of the first two months, the group treated with streptomycin showed a much higher recovery rate than the group receiving bed-rest only, but at the end of the sixth month, this difference had become much smaller, a higher proportion of the controls and a lower proportion of the treated cases showing recovery. Had the controls not been included in the trial, streptomycin would have been given credit for the recoveries which actually were due to bed-rest alone, and the decline in the efficacy of the drug would not have been so readily detected. The reason for this decline is that the tuberculosis

organisms acquire resistance to streptomycin and cannot then be eradicated. For this reason, the report recommends that streptomycin should only be used in certain types of pulmonary tuberculosis, the possible advantages of the treatment being weighed against the danger of producing a streptomycin-resistant strain and eventually perhaps a future public health problem. C. Wilson<sup>50</sup> has reported the successful use of streptomycin in certain non-tubercular conditions. In the U.S.A., the Council on Pharmacy and Chemistry have summarised the results obtained in a large series of cases<sup>51</sup> and concluded that the value of streptomycin has been established in certain types of pulmonary tuberculosis, in tuberculous meningitis, in acute miliary tuberculosis and in tuberculous infections in various sites. In view of the large number of such cases and the fact that the dose is 1-2 g. per day, it will be appreciated that the potential demand for the drug is considerable. As already stated, production in the U.S.A. is now on a substantial scale, and five or six firms are in operation. At present only one firm in this country is in production.

*Streptomycin fermentation.*—In the Annual Report for 1945, it was recorded that streptomycin is made by submerged culture of *Streptomyces griseus* in a medium containing a nitrogen-rich source such as peptone, casein or corn steep liquor and a source of carbon such as glucose or glycerol. Its isolation by adsorption on carbon and elution of the adsorbate with acid alcohol and its purification via the helianthate or reineckate were also referred to. Little further information has been published since, although it has been shown that on a medium containing glucose, meat extract, peptone, and common salt, carbon, nitrogen and phosphorus are removed rapidly from solution during the first half of the fermentation cycle with a correspondingly high oxygen consumption, but with little streptomycin formation.<sup>52</sup> Thereafter autolysis occurs, mycelium production falls with liberation of nitrogen and phosphorus into the medium and formation of streptomycin. Ammonia-nitrogen, but not nitrate-nitrogen, is utilised by the mould, potencies of 150 units per ml. being obtained with ammonium phosphate as the sole source of nitrogen<sup>53</sup>; small amounts of corn steep liquor, casein-digest or soya bean meal increased the titres. Of several organic nitrogen compounds tested, six amino acids gave yields in excess of 100 units per ml. and one, L-proline, gave a titre of 800 units per ml., but it was no use as a supplement to other nitrogen sources. Wheat bran is claimed to be of value in the streptomycin fermentation, the ash being responsible for the effect.<sup>54</sup> A synthetic medium consisting of glucose, lactic acid, ammonia-nitrogen, potassium, magnesium, and phosphate is said to give over 400 and 250 units per ml. by surface and submerged growth respectively.<sup>55</sup>

*S. griseus* is an extremely variable organism, and care must be taken to prevent streptomycin-producing strains from losing this property. Indeed, any ordinary culture will give rise to a number of variants, some of which do not produce streptomycin.<sup>56</sup> On the other hand, improved strains may occasionally result. A good strain was obtained from the soil of Bikini Atoll and has been given a specific name, *S. bikiniensis*.<sup>57</sup> Again, by selection of a normal strain, giving 100-200 units per ml., a strain giving 400-500 units per ml., was obtained; after ultra-violet irradiation, a mutant giving 900 units per ml. was isolated.<sup>58</sup>

*Isolation and purification.*—There is nothing further to report on methods of isolation, but considerable progress has been made in methods of purification. Hitherto streptomycin for clinical use has been supplied as the amorphous hydrochloride or sulphate. Recently a crystalline double salt of the hydrochloride with calcium chloride, first reported in 1945, has been marketed. This is made by allowing the two components to react in a solvent in which both are soluble, *e.g.*, methanol, and evaporating until crystallisation occurs.<sup>59</sup> More recently, the trihydrochloride of streptomycin was obtained in crystalline form from methanol solution; it analyses as a dihydrate with a potency of 820 units per mg.<sup>60</sup>

*Assay.*—The normal procedure for assaying solutions containing streptomycin is similar to that used for penicillin, the solution being put into cups or holes in an agar plate seeded with a suitable test-organism. In an attempt to increase the number of tests that can be carried out per day, K. A. Brownlee *et al.*<sup>61</sup> devised a method involving the use of large plates instead of Petri dishes. Chemical and physical methods are also available for the assay of streptomycin, namely a polarographic method<sup>62</sup>; a method based on the formation of maltol by alkaline hydrolysis<sup>63</sup>; a colorimetric method involving the use of a coloured semi-carbazide<sup>64</sup>; and a fluorimetric method involving the use of 9-hydrazino-acridine hydrochloride.<sup>65</sup>

Streptomycin, like benzylpenicillin, appears to be formed along with substances of similar chemical and antibacterial properties, and at least five different antibiotics have been demonstrated in purified streptomycin by paper chromatography; even the calcium chloride complex was not homogeneous.<sup>66</sup> Streptomycin B is the best known of these substances. It was separated from streptomycin by chromatography and purified as the reineckate<sup>67</sup> and converted into a crystalline trihydrochloride with a potency of about 210 units per mg.<sup>60</sup> It was identified as a mannosido derivative of streptomycin,<sup>68</sup> from which it can be distinguished by means of a 0.2% solution of anthrone in 95% sulphuric acid; the same reagent can be used for its estimation.<sup>69</sup>

*Chemistry of streptomycin.*—There is nothing further to add to the information given in previous years' Reports, except that the formula given in the 1947 Report is now generally accepted, conclusive proof having been obtained that the streptobiose chain is linked glycosidically at position 4 of the streptidine molecule, and not at position 5.<sup>70</sup> Streptidine has been synthesised.<sup>71</sup>

*Presentation.*—The toxic manifestations reported in the early days of streptomycin treatment are now seldom encountered, owing to the increased purity of the drug now in use and to a reduction of the dosage from 3 to 2 or even 1 g. of base per day. Any method of improving the effectiveness of streptomycin, especially by reducing the tendency of organisms to become streptomycin-resistant would be of outstanding value, but the only variation so far reported in the method of administering the drug is its use in conjunction with other antibacterial agents. Promising results have been reported in the treatment of tuberculosis with a mixture of streptomycin and "Sulphetrone,"<sup>72</sup> *p*-aminosalicylic acid<sup>73</sup> or potassium iodide.<sup>74</sup> Dihydrostreptomycin, which is made by catalytic hydrogenation of streptomycin,<sup>75</sup> is being placed on the market;

it is said to be better tolerated than the parent compound. Unfortunately it also induces drug-resistance.

### Other Antibiotics

It is not easy to select from among the large number of known antibiotics the probable successors to penicillin and streptomycin. Because they are effective against organisms for which there is at present no known chemotherapeutic agent, it seems justifiable to single out for special mention chloromycetin, aureomycin, and a few other substances, although their clinical value has not been unequivocally established.

*Chloromycetin*.—An organism closely related to *Streptomyces lavendulae* was found to produce a chlorine-containing antibiotic, which could readily be isolated in crystalline form by extraction with ethyl acetate, evaporation of the extract, extraction of the residue with ether and chromatography of the ethereal extract on alumina.<sup>76</sup> The organism was isolated from a field in Venezuela and has therefore been named *S. venezuelae*<sup>77</sup>; the same or a similar organism has since been isolated from soil on a farm in Illinois. Chloromycetin had no effect *in vitro* on yeasts, filamentous fungi and protozoa, but was moderately active on Gram-positive bacteria and *Mycobacterium tuberculosis* and particularly active against Gram-negative bacteria.<sup>78</sup> It had no effect *in vivo* on avian malaria, rabbit syphilis, gonococcal or streptococcal infections in mice or against type A influenza, St. Louis encephalitis, and rabies in mice, but it gave moderate protection against *Klebsiella* and *Shigella* infections in mice and remarkable protection against *Rickettsia prowazeki* in chick embryos. Its toxicity is similar to that of streptomycin. The compound is very sparingly soluble in water, but can be administered either parenterally in propylene glycol or orally. Its effectiveness against viruses and rickettsiae has been confirmed by J. S. Smadel and his colleagues, and it is specially active against the viruses of psittacosis and lymphogranuloma venereum.<sup>79</sup> It has recently been used successfully in the treatment of scrub typhus, the bane of jungle fighters in the Burma campaign, and in ordinary typhus.<sup>80</sup> No toxic effects are produced by administration of chloromycetin to normal humans.<sup>81</sup>

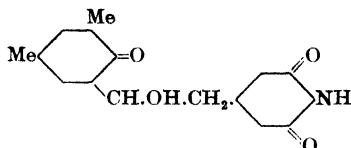
Chloromycetin is said to have been synthesised, but no details have been published.

*Aureomycin*.—The second antibiotic to show promising results against virus infections is aureomycin, produced by *Streptomyces aureofaciens*. No details concerning the fermentation or the method of isolation have been published.

Aureomycin is active *in vitro* against many bacteria, including penicillin- and streptomycin-resistant organisms,<sup>82</sup> whilst *in vivo* it is active against the viruses of lymphogranuloma venereum<sup>83</sup> and psittacosis.<sup>84</sup> It has been used successfully in humans for the treatment of lymphogranuloma,<sup>83</sup> Rocky Mountain spotted fever, due to *Rickettsia rickettsii*,<sup>85</sup> ocular infections due to various organisms,<sup>86</sup> primary atypical pneumonia, brucellosis, and urinary tract infections with organisms of the *coli-aerogenes* group,<sup>84</sup> and it is being tested in typhoid fever. It does not appear to induce drug-resistance easily.

*Other Streptomyces antibiotics.*—As already noted, *S. griseus* is a very variable organism and it, and closely related species, appear to be capable of producing a number of antibiotics, some with closely related biological and possibly chemical properties, others differing considerably from one another in both respects.

An antibiotic sometimes produced by *S. griseus* at the same time as streptomycin is actidione, a neutral substance inactive against bacteria, but highly active against yeasts,<sup>87</sup> including the pathogenic yeast, *Cryptococcus neoformans*. It is readily isolated from the culture fluid or mycelium by extraction with ether or other organic solvent. Its chemical structure is probably<sup>88</sup>:



The yields of streptomycin and actidione vary independently of one another with variations in the nature of the medium, and mutation of the organism may affect one and not the other, though generally the yields of both antibiotics are reduced.

Another antibiotic produced by certain strains of *S. griseus* is grisein.<sup>89</sup> This substance inhibits the growth of streptomycin-resistant organisms; it can be detected and assayed by means of streptomycin-resistant *E. coli*. It is active *in vivo* against organisms that are sensitive to it *in vitro* and its toxicity is low. Like actidione, it is neutral, possessing no basic or acidic groups.

*S. lavendulae* produces an antibiotic, "Antibiotic 136," which differs from streptothricin in its anti-bacterial spectrum and greater toxicity to mice.<sup>90</sup> Streptolin, produced by another *Streptomyces*, closely resembles streptothricin in anti-bacterial and chemical properties, but is more toxic; it forms a crystalline helianthate.<sup>91</sup> Xanthomycins A and B are two more *Streptomyces* antibiotics, which are, however, very toxic; the former, but not the latter, yields a crystalline helianthate.<sup>92</sup> Sulfactin, another *Streptomyces* antibiotic, is effective against *Diplococcus pneumoniae* infection in mice and relatively non-toxic.<sup>93</sup> Musarin is a particularly potent antifungal antibiotic produced by Meredith's actinomycete. It derives its name from the fact that it is of value in combating Panama disease of the banana plant (*Musa*) due to *Fusarium oxysporum* var. *cubense*. It has the empirical formula  $(C_{35}H_{66}O_{14}N_2)_{72}$ .<sup>94</sup>

*Subtilin and bacitracin.*—Amongst the first antibiotics to be discovered were two bacterial products, gramicidin and tyrocidine, but they were eclipsed in importance by the mould antibiotic, penicillin, and the *Streptomyces* antibiotic, streptomycin. Interest in bacterial antibiotics has revived, however, with the discovery of subtilin and bacitracin, both produced by *Bacillus subtilis*. The former was obtained from both the culture fluid and pellicle when the organism was grown on a medium containing molasses, grain worts or corn steep liquor, or, best of all, asparagus butt press juice.<sup>95</sup> Isolation from the pellicle was effected

by extraction with 70% alcohol, evaporation, and extraction of the residue with stronger alcohol. The substance was mainly active against Gram-positive organisms.<sup>96</sup>

Bacitracin was extracted from the culture fluid by *n*-butanol and partially purified by adsorption of impurities on magnesia.<sup>97</sup> It was less effective than subtilin against *Streptococcus pyogenes*, but more active against *Treponema pallidum*.<sup>98</sup> Like many other bacterial antibiotics bacitracin is a polypeptide; it consists of phenylalanine 11%, leucine 9%, isoleucine 22%, glutamic acid 10%, aspartic acid 17%, lysine 9%, histidine 10%, cystine 14%, and ammonia 1.5%.<sup>99</sup>

Other antibiotics produced by *B. subtilis* are Subtilin C, extracted from the pellicle by means of aqueous alcohol and active against Gram-positive, but not Gram-negative, organisms, and only slightly active against *M. tuberculosis*<sup>100</sup>; subtenolin, similar in its anti-bacterial properties to Subtilin C<sup>101</sup>; and bacillomycin with almost complete lack of anti-bacterial activity but with marked antifungal properties.<sup>102</sup>

*Polymyxin : Aerosporin*.—Polymyxin is the name given to an antibiotic produced by *Bacillus polymyxa* and isolated from the culture fluid by adsorption on charcoal and elution with acid methanol and purified *via* the picrate.<sup>103</sup> A similar substance was isolated by a similar procedure from the culture fluid produced by *B. aerosporus*<sup>104</sup> and given the name aerosporin. It had no action on *M. tuberculosis*, but gave complete protection to animals infected with *H. pertussis*, *S. typhi*, *H. bronchi-septicus*, and *E. coli*. It was more toxic than streptomycin. It gave promising results in preliminary trials with whooping cough in children.<sup>105</sup>

On hydrolysis aerosporin gave a mixture of amino acids.<sup>106</sup> So did polymyxin,<sup>107</sup> and the two compounds proved to be closely related in chemical and biological properties.<sup>108</sup>

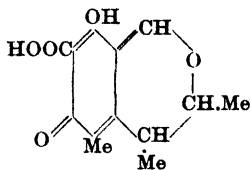
*B. aerosporus* and *B. polymyxa* are now regarded as identical organisms, yielding a group of antibiotics known collectively as the polymyxins.<sup>109</sup> Each of the five members characterised so far contains three of four amino acids, one of which,  $\alpha$ -diaminobutyric acid, has not previously been reported to occur in nature. This and threonine occur in all the polymyxins together with either leucine, phenylalanine or sérine. Three of them yielded an optically active fatty acid after hydrolysis.

An antibiotic has been obtained from *Bacillus lurva*, the organism responsible for American foul brood disease of bees,<sup>110</sup> but nothing has been reported about its anti-bacterial properties. *Bacillus cereus* produced an antibiotic active against both Gram-positive and Gram-negative bacteria.<sup>111</sup>

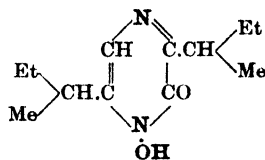
*Miscellaneous mould antibiotics*.—The importance of moulds as sources of antibiotics has declined considerably in recent years, for the most promising substances recently discovered have been obtained from either actinomycetes or bacteria. Recent publications on mould antibiotics are concerned almost entirely with their chemical constitution or synthesis, matters of somewhat academic interest since the substances themselves appear to have no clinical value.

The constitution previously assigned to citrinin, an antibiotic produced by *Penicillium citrinum*, has been questioned by D. J. Cram,<sup>112</sup> who suggests three other formulae. None of these, however, agrees with the structure

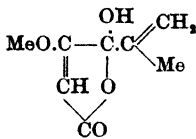
(I) assigned to it by A. Robertson and his colleagues,<sup>118</sup> who claim to have synthesised a substance with this structure and found it to be identical with citrinin.



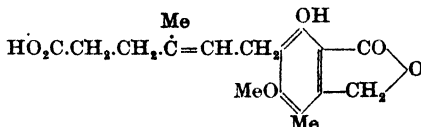
I.



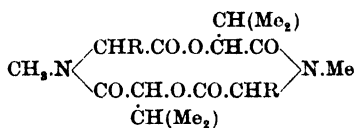
II.



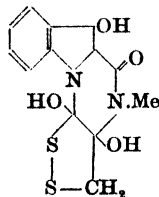
III.



IV.



V.



VI.

Aspergillie acid, produced by *Aspergillus flavus*, has been given formula II,<sup>114</sup> whilst mycelianamide, which is produced by *Penicillium griseo-fulvum* and is inhibitory to Gram-positive, but not Gram-negative, bacteria, is believed to be the amide of O-mycetyl-N-pyruvyl- $\beta$ -ketotyrosine.<sup>115</sup> The synthesis of penicillic acid,<sup>111</sup> the anti-bacterial metabolite of *Penicillium puberulum* and *P. cyclopium* has been announced.<sup>116</sup> Mycophenolic acid, from *Penicillium brevi-compactum*, has been given formula IV.<sup>117</sup> Enniatin A, produced by *Fusarium orthoceras*, has been given formula V, R = CHMe.C<sub>2</sub>H<sub>5</sub>, and Enniatin B, formula V, R = CH<sub>2</sub>.Me.<sup>118</sup> They are probably identical with the corresponding lateritiins, produced by *F. lateritium*.<sup>119</sup> Gliotoxin, produced by both *Aspergillus fumigatus* and *Penicillium obscurum*, has been given formula VI.<sup>120</sup>

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# ESSENTIAL OILS, ISOLATES AND DERIVATIVES

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THE year 1948 will have been a memorable one to all who are interested in essential oils since it has seen the publication of two books devoted to the subject; the first being entirely new and the second, an old friend, revived. "The Essential Oils," Vol. I, by E. Guenther,<sup>1</sup> is the forerunner of a number of volumes by an acknowledged authority upon the subject in collaboration with a panel of experts in the various sections treated. That such a work is necessary will be realised when one considers that no comprehensive book has been published on essential oils for about 20 years. The Schimmel Report 1945,<sup>2</sup> which before the war emanated from the Miltitz headquarters of the Schimmel organisation, has been sorely missed since 1939. The 1945 volume of 127 pages was issued this year by Schimmel Co. Inc., of New York, and takes the well-known form of its predecessors. It is divided into four sections which deal with commercial and scientific developments in essential oils and related materials, research in the field of aromatics, statistical notes and a bibliography. To those concerned with medicinal oils the publication of a new edition of the British Pharmacopoeia<sup>3</sup> is always an important event. The 1948 Pharmacopoeia contains monographs for 17 essential oils which show few significant changes from those of the 1932 publication and its Addenda. In the case of oil of lemon, however, the aldehyde content, which was lowered temporarily in the seventh addendum, has been raised to the original figure of 4%. Oil of Siberian Fir and the two Sandalwood oils are no longer official. In the 1948 monographs the term specific gravity has disappeared in favour of "weight per ml." Since minimum standards are laid down for the essential oil content of certain drugs it has been necessary to include in an appendix an official method for the determination of this figure which is expressed as a percentage v/w. Aromatic waters prepared by distillation are no longer included in the Pharmacopoeia, such waters now being prepared either by solution of the oil in water or by dilution from concentrated waters.

The utilisation of the resources of the Empire, the U.S.A., and other parts of the world continues to engage the attention of numerous workers in the field of essential oils. In New South Wales<sup>4</sup> seeds of *Melaleuca viridiflora* were collected and the seedlings cultivated at National Park, near Sydney. When three years old, the trees were cut down and the foliage distilled, yielding 1.7–2.6% of an oil having the characters:  $d_{4}^{20}$ , 1.4720–1.4763;  $\alpha_D$  (100 mm. tube) + 13.3– + 14.6;  $n_{D^{20}}$ , 0.8806–0.8857; ester value 2.8–4.8; ester value after acetylation 163–193. Apart from a trace of benzaldehyde in the first runnings the oil consisted of a simple binary mixture of about 30% linalool and 70% nerolidol. As with other Australian trees there are indications that this species exists

in a number of physiological forms which yield oils of different composition, but by careful selection varieties containing a high proportion of these two useful alcohols may be secured. Oil from the leaves and terminal twigs of *Melaleuca bracteata* F.v.M. distilled in Kenya has been examined at the Imperial Institute and also in the laboratories of an English distiller. Cosgrove, Islip, and Thain<sup>5</sup> considered, from analytical data, that the oil had the approximate composition: aldehydes (mainly cinnamic) 1.0; phenols (mainly eugenol) 1.7; acids (mainly cinnamic) 0.3; free alcohols (probably tertiary, as  $C_{10}H_{18}O$ ) 2.0; esters (calculated as cinnamate of  $C_{10}H_{18}O$ ) 11.7; phenol ethers (methyl-eugenol) 82.0; undetermined (terpenes and sesquiterpenes) 1.3% w/w. In the opinion of the authors the commercial prospects of the oil, which resembled closely Huon pine oil (*Dacrydium franklini*), were somewhat doubtful, although a market might be found as a source of methyl-eugenol. Mitchell,<sup>6</sup> after examination of an oil from the same source, suggested the following composition: methyl-eugenol 75.0; phenols (mainly eugenol) 1.7; terpenes 6.5; free acids (mainly cinnamic) 0.5; combined acids (mainly cinnamic) 4.0% w/w and aldehydes (probably cinnamic) a trace. The opinion is expressed that while this oil could form a good source of methyl-eugenol it is unlikely to be of commercial importance since methyl-eugenol is readily prepared by methylation of eugenol. Menon and Ittyachan<sup>7</sup> have reviewed the distribution and cultivation of Vetiver root and also the extraction of the oil in India. At present, the yield of oil by steam distillation varies between 0.152 and 0.495%, but this could be considerably increased by improved methods. Solvent extraction gave an oil which was superior in aroma to the distilled oil. The need for improvement in the industry is stressed.

The production, in the U.S.A., of oils of cedar leaf, cedar wood, erigeron, pennyroyal, sassafras, sweet birch, and wintergreen obtained from wild plants and of dill, lemongrass, tansy, wormseed, and wormwood from cultivated plants are discussed by Sievers.<sup>8</sup> In a report covering a four-year study of peppermint oils from various districts of Washington and Oregon, Tornow and Fischer<sup>9</sup> have tabulated the characters of these oils. An account of *Pycnanthemum pilosum* (Mountain mint) is given by Pellett.<sup>10</sup> This plant grows naturally on soils of low fertility in Missouri, and an experimental plot produced oil at the rate of 200 lb. per acre. About 50% of its weight of menthol or thymol could be recovered from the oil. Lavender cultivated experimentally in Oregon is claimed by Pease "to yield an oil which is comparable with the English oil." Twenty-five species of cedar are discussed by Klein<sup>12</sup> from the point-of-view of their economic importance. The production of cedarwood oil from *Juniperus virginiana* and *J. mexicana* is described and the properties of the oils from these two woods are tabulated. The distillation and composition of the volatile oil from a petroleum spirit extract of pine stumps and the economic uses of the various terpenes obtained from the oil is the subject of an article by Clark.<sup>13</sup> The geographical distribution of citrus fruits, the anatomical structure and extraction of the oils are discussed by Stormont.<sup>14</sup> The yield of oil varies with the maturity and condition of the fruit, but average figures are quoted per 1000 fruit as 20 oz. from oranges, 16 oz. from lemons, and 18 oz. from limes. Various

methods of concentration of citrus oils are described in a paper by Lakritz.<sup>15</sup>

Fonseca<sup>16</sup> has determined the content of essential oil in the leaves of *Artemisia absinthium* of varying ages and seasons. On the basis of dry weight, young leaves yielded 0.34–0.38% when collected in November and 0.41% in July. The corresponding values for fully grown leaves were 0.15–0.20 and 0.38% respectively. It is suggested that only leaves collected in winter be used for drug purposes and that the minimum standard of essential oil content be set at 0.20%.

Before the war the forest services of Indo-China<sup>17</sup> had undertaken a certain amount of re-afforestation, including plantings of coniferae. The species common in the region are *Pinus merkusii*, *P. tonkinensis*, *P. massoniana*, *P. khas-ya*, and *P. langbianensis*. Oleo-resin of *P. merkusii* gave 21.5% of turpentine and 75% of resin which is distinctly above the average. The cinnamons of Indo-China occur in several varieties; Yen-Bay, Thang-Hoa (Royal Cinnamon), and Annam cinnamon, which appear to be all from *Cinnamomum obtusifolium* sub-var. *laureiri*. Yields of oil range from 1.07–3.25% from bark of stems and branches. The cinnamic aldehyde content of the oil is 80–95%. It is considered that there are great possibilities for developing and improving bark and oil production in Indo-China.

In a report on some work carried out in the laboratories of L. Givaudan and Co., Y. R. Naves<sup>18</sup> states that oil distilled from the whole plant while in fruit of *Diplophium africanum* Turcz. was obtained in Tanganyika in a yield of 1%. The principal constituent was a bicyclic ketone,  $C_{10}H_{16}O$ , which was dextro-rotatory. *Acolanthus graveolens*, a labiate common in Rhodesia and Tanganyika, yielded an oil consisting mainly of a mixture of geraniol and nerol. Two samples of *Eucalyptus staigeriana* R.v.M. oil from Seychelles contained about 35–50% limonene dipentene, *E. macarthuri* Dean and Maiden, from the Belgian Congo, appeared to be a product of incomplete distillation since eudesmol and nerol were almost entirely absent, but it contained about 40% of geraniol. *Leptospermum flavescens* Sm. var. *citratum* oil from Rhodesia contained citral citronellal 74%, alcohols as  $C_{10}H_{18}O$ , 8.2%. Ceylon citronella oil contained stereochemically pure 1-borneol and the citronellal was only slightly racemised,  $\alpha_D^{20} = +12.1$ – $+12.6$ , and the camphene content was 5–6%. A lemongrass oil from Guatemala, distilled from *Cymbopogon flexuosus* Stapf. contained in the heavy fractions about 0.7% of a diterpene ketone.

A useful review is given by la Face<sup>19</sup> of the production in Italy and Sicily of citrus oils and also of the cultivation of *Jasminum officinale*, *Geranium tuberosum*, *Acacia farnesiana* Rosa spp. *Ocimum basilicum*, *Origanum majorana*, *Pinus sylvestris*, *Thymus serpyllum*, *Lavandula vera*, *Rosmarinus officinalis*, *Salvia officinalis*, *S. sclarea*, *Mentha pulegium*, and *Myrtus communis*. In a monograph by d'Argila<sup>20</sup> a comprehensive account is given of the production in Spain and also of the uses of aniseed (*P. anisum* L.), aniseed oil, and anethol.

The problem of the production of essential oil in jasmin blossoms has brought forward a number of theories which are discussed by Naves.<sup>21</sup> That the last word has not been pronounced on this subject is evident

from the author's concluding comment—"up to the present, all attempts to explain the continued formation of essence of jasmin during the lifetime of the blossom have ended in complete failure."

A further contribution to the theory of fixation of perfumes is made by Ruemele,<sup>22</sup> who suggests that the action of fixatives may be dependent upon their ability to increase the viscosity of perfumes. The citrus oils, which are of low viscosity, are unstable while patchouli, sandalwood, vetivert, styrax, amyl salicylate, and ionone are more stable.

### Composition and characters

*Acorus calamus* L.<sup>23</sup>—The essential oil contents of di-, tri-, and tetraploid types of *A. calamus* were found to be 2.17, 3.12, and 6.82% respectively, but there was no significant difference in the water-contents. The oil content of the diploid *A. gramineus* Sol. was 0.7% in both the green-leaved and variegated varieties.

*Agathosma gnidioides* Schlechter.<sup>24</sup>—The fresh leaves of this South African plant yielded in summer 0.6, in autumn 0.7, and in winter 1.0% of oil containing myrcene, (–)- $\beta$ -pinene, (–)-limonene, dipentene, (–)-linalyl *iso*-butyrate, bis-(1-pentenyl-2) tetrasulphide,  $C_{10}H_{18}S_4$ , butyric, and *iso*-butyric acids, (+)-linalool, salicylic acid, and methyl salicylate.

*Allium cepa*.—Essential oil of onion<sup>25</sup> had a retardant action on the growth of bacteria and the germination of seeds. In a concentration of 1 in 1,000 it had a very favourable and rapid effect on catarrhal conditions. Vacuum distillation of minced onions<sup>26</sup> at room temperature gave a clear nitrogen-free distillate containing a lachrymatory principle, but which on standing became milky. Distillation of the milky fluid gave a gummy residue containing 43% S, corresponding to thiopropaldehyde or thioacetaldehyde.

*Artemisia austriaca*.<sup>27</sup>—The fresh plant yielded 0.15% of a camphoraceous oil containing cineol, phellandrene,  $\alpha$ - and  $\beta$ -thujones, thujyl alcohol, and esters with stearic and palmitic acids.

*Artemisia scoparia* Waldst. and Kit.<sup>28</sup>—The green herb and flowering heads of this Indian herb yielded 0.75% of essential oil containing eugenol 8.96%, a sesquiterpene, scoparilene 79.44%, and a hydrocarbon 2.63%.

*Bassia longifolia*.<sup>29</sup>—fruit on steam distillation gave an oil containing ethyl cinnamate 22.72,  $\alpha$ -terpineol 3.53, and sesquiterpenes and sesquiterpene alcohols 67.87%

Dried leaves of *Cinnamomum zeylanicum*<sup>30</sup> yielded 2% of oil with a eugenol content of 70–90%.

Post-war deliveries of Java Citronella oil<sup>31</sup> are stated by Sparenburg to be of lower quality than pre-war material. Determination of citronellal by treatment with  $NH_4OH$  in weakly-acid or neutral media gave rather lower results ( $\sim 2$ –3%) than the standard method employing an alkaline medium, due to ketonic impurities not present in fresh oils. Some recent samples have contained *isopulegol* up to 10% and methylheptenole.

*Citrus decumana*<sup>32</sup> leaves on distillation yielded a fragrant yellow oil having the composition (+)- $\alpha$ -pinene 2.6, (–)- $\beta$ -pinene 6.6, linalool 42.34, linalyl acetate 44.18, and an unidentified residue 4.28%.

*Citrus limonia* var. *acida*, "Galgal."<sup>33</sup>—The fresh fruit grown in India yielded 0.9% of a pale yellow oil containing (+)-limonene 92.24, citral 3.6,  $\alpha$ -terpineol 0.64, wax 0.37%, and the valeric ester of a sesquiterpene alcohol.

*Dacrydium kirkii*<sup>34</sup> leaves collected in September and November gave an oil containing (+)- $\alpha$ -pinene 65, myrcene 4, (+)-limonene 2, unidentified terpenes 2, cadinene 1, unidentified sesquiterpenes 1.5, phyllocladene 1, unidentified sesquiterpene alcohols 5.5, (+)-bornyl acetate 1%, and a trace of carvone.

During an examination of the residues from commercial eucalyptus oils Ralph<sup>35</sup> isolated a number of minor constituents. *E. dives* oil contained methyl cinnamate, geranic acid and eudesmol. *E. australiana* contained methyl cinnamate, geranic acid, and some cinnamic acid. During distillation of piperitone from *E. dives* oil a crystalline material, *p*-menthane-1 : 2 : 3-triol separated.

*Eucalyptus cneorifolia*.<sup>36</sup>—Oils distilled in Australia in December 1943 were found to be exceptionally high in terpenes (average 58%), and contained less than 1% of cymene. The presence of  $\alpha$ - and  $\beta$ -phellandrene and also of small amounts of dipentene were confirmed.

*Juniperus mexicana*.<sup>37</sup>—The oil of this species of cedarwood was found to be superior in strength of odour, persistence and bouquet to that of *J. virginiana*. It is considered that the wide distribution of the species in Texas, throughout Mexico to Guatamala is an assurance of raw material for an indefinite period.

*Lavandula viridis*.<sup>38</sup>—Fresh flowering tops of this lavender distilled in Portugal yielded 0.5–0.8% of oil with *d*, 0.9239; *n*<sub>D</sub>, 1.4745;  $\alpha_D^{20}$  50'. and the approximate composition: terpene hydrocarbons ( $\alpha$ -pinene camphene, etc.) 20, cineole 30, alcohols (borneol, geraniol) 26, esters 5, ketones (camphor) 5, and undetermined 14%.

Indian Linaloe<sup>39</sup> oil distilled from *Bursera depechiana* or *B. aloexylon* (commonly known as the Mexican linaloe tree) was found to contain methylheptenol 1.5, linalool 47.7, and linalyl acetate 40.8%.

*Lippia asperifolia* (*Verbena capensis*).<sup>40</sup>—Flowering tops of this plant from Tanganyika yielded 0.4% of oil containing about 80% of ocimene and a mixture of ketones, C<sub>10</sub>H<sub>14</sub>O, of the dehydrotagetone series (ocimene, myrcenone, and others).

*Melia azadirachta* L.<sup>41</sup>—An essential oil distilled from the ether extract of the flowers was fractionated and the characters of the fractions recorded.

*Mentha rotundifolia*.<sup>42</sup>—Fresh tops yielded 0.05–0.097% of oil with *d*, 0.960–0.975;  $\alpha_D^{20}$  –24°; *n*<sub>D</sub> 1.475–1.484, ester value 101–133; ketones (as menthone) 1.84%.

*Micromeria abyssinica* (Hochst.) Benth.<sup>43</sup>—The essential oil was found by Naves to consist largely of (+)-isomenthone and (+)-pulegone.

*Narcissus poeticus* L.<sup>44</sup>—The distillable fraction of the concrete oil was found to contain as chief constituents, eugenol, benzaldehyde, benzoic acid free or esterified, benzyl and cinnamyl alcohols. The aromatic constituents responsible for the characteristic odour were not determined.

*Ocimum gratissimum*.<sup>45</sup>—The oil of this plant obtained from the Society Islands consisted of eugenol 61.8, other phenols 17.4, ocimene, sesquiterpenes, and other non-phenolic compounds 20.8%.

*Ocimum kilimandscharicum*.<sup>46</sup> known in Kenya as the "camphor basil" was cultivated as an annual in the Boston area and on distillation of the dried leaves 2.5% of oil and 2.54% of camphor were obtained.

The hand-pressed peel oil of Sylhet oranges<sup>47</sup> was found to have the composition: (+)-limonene 94.14%, terpinene, a trace; methyl anthranilate 0.2% and wax 0.56%.

*Paesia scaberula* (New Zealand Scented Fern).<sup>48</sup>—Fronds collected in the autumn and steam distilled gave 0.05% of a deep red oil which showed a deposit on standing of a crystalline paraffin. A sesquiterpene alcohol,  $C_{15}H_{24}O$ , and a paraffin, *n*-heptacosane, were also isolated.

*Phyllocladus trichomanoides*.<sup>49</sup>—The winter oil from the leaves and terminal branches of this Australian plant was obtained in 0.2% yield. The characters were *d* 0.9031,  $\alpha_D$  16.29,  $n_D$  1.4855. Only traces of acids, esters, or alcohols were present. Aldehydes and phenols were absent.

The volatile oil of rice embryo<sup>50</sup> was examined in Japan and found to contain 90% of paraffin hydrocarbons ( $C_{10}$ – $C_{15}$ ), aromatic hydrocarbons (mono- and *p*-di-alkyl benzenes), naphthalene, *p*-methyl naphthalene, and dimethylnaphthalene together with caproic and capric acids.

*Salvia sclarea* L.<sup>51</sup>—A review of the history, botany, and uses of this plant and also the composition of the volatile oil is given by Rovesti.

*Shorea robusta* ("Chua" oil).<sup>52</sup>—Dry distillation of this Indian resin yielded 62% of volatile oil containing homocatechol mono-ethyl ether 0.46; 3-methoxy-4-propylphenol 0.53; 3-methoxy-4-ethylphenol 0.3; 3-methoxy-4-ethoxytoluene 9.38; 3:4-dimethoxy-1-propylbenzene 15.88; homocatechol dimethyl ether 4.78%.

*Thymus caespitosus*<sup>53</sup> yielded 0.268–0.52% of oil containing esters 8.3–10.4%, free alcohols 42–46%, phenols 3–4%, pinene, cadinene, and ( $\pm$ )- $\alpha$ -terpineol.

*T. capitellatus*<sup>54</sup> yielded 0.9% of oil containing (–)-borneol 30%, cineole 30%, phenols 3.5%, pinene, camphors, an unidentified alcohol, and esters of isovaleric acid.

*T. mastichina*<sup>55</sup> oil contained cineole 60%, phenols 2%, pinene, linalool, and ( $\pm$ )- $\alpha$ -terpineol.

*T. villosus*<sup>56</sup> yielded 0.6% of oil containing esters 28%, free alcohols 37%, and phenols 5%.

*T. zygis* subsp. *sylvestris*<sup>57</sup> yielded 0.16% of oil containing thymol 8.5–9.3%, cineole 13%, carvacrol 3%. Oil of *T. zygis* var. *alphagracilis* contained thymol 16% and carvacrol 6%.

*Vetiveria zizanioides*.<sup>58</sup>—The habitat, cultivation, and propagation of this plant are discussed. Oils examined had the range of characters: *d* 0.9964–0.9780; acid value 9–21; ester value 10–22; solubility in 80% alcohol 1.25–2 vols.

*Vitex negundo*.<sup>59</sup>—Fresh leaves of this Indian shrub yielded 0.04–0.07% of a greenish yellow oil containing 22.5% of aldehydes and ketones, 15% of phenolic derivatives and 10% cineole.

### Isolates and derivatives

A number of halogenated terpenes were examined with a view to determining their insecticidal value.<sup>60</sup> The principal products tested were bornyl chloride, dichlorodipentene, tricyclene chloride, and dichlorocymene. These were tried on the haricot weevil (*Acanthoscelides obsoletus*), dog flea (*Pulex serraticeps*), pig louse (*Hematopinus suis*), and some ticks (*Ixodidae*). Activity appeared to be largely determined by solubility in lipoids and relative instability of the chlorinated molecule; the insecticidal effect being probably due to the formation of HCl. There was a wide variation in action as between the different isomers. Tricyclene chloride and dichlorocymene were not very effective against the haricot weevil; but if used as solvents for DDT or H.C.H. the effect of these latter was enhanced. These two chlorinated terpenes were very effective against the common house-fly and the Colorado beetle.

Klosa<sup>61</sup> found that the aqueous steam distillate from thyme, after separation of the oil, had a retardant effect on the germination of seeds (peas) and, as have similar distillates from chamomile and yarrow, had an anti-bacterial action in cases of infectious skin diseases and wounds.

Naves<sup>62</sup> starting with 2 : 3-dimethylbutadiene has prepared 3-methyl-7 : 8-dihydrolinalool. Oxidation by Beckmann's chromium oxide mixture gave a good yield of mixed 3-methylcitral. 3-Methylgeraniol was obtained by boiling methylalool with acetic anhydride and then saponifying with alcoholic KOH. Mixed methylionones were obtained from 3-methyl citral by condensation with acetone and cyclisation of the condensation products. They were also obtained from 3-methylgeraniol by treatment with aluminium tertiary butylate.

The constitution of the "camphor" ( $C_{15}H_{26}O_2$ )<sup>63</sup> which crystallises from the high-boiling fractions of calamus oil has been partially elucidated.

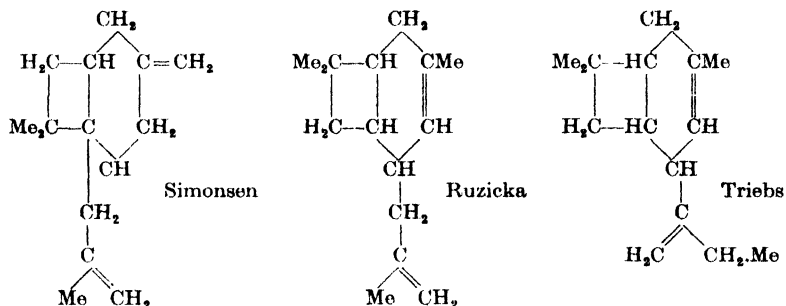
Clark,<sup>64</sup> in a review of the literature covering the extraction, synthesis, and chemical structure of azulenes has reduced their number to five—S-guaiazulene from guaiacum wood, callistris, patchouli, gurjun balsam, eucalyptus, and geranium; camazulene from chamomile and yarrow; lactarazulene from *Lactarius deliciosus*; elemazulene from elemi and vetivazulene from vetiver.

Analyses of bezoars<sup>65</sup> showed them to contain, in addition to proteins, fats, gums, sulphur, and mineral matter, a number of odorous constituents, including indole, skatole, and muscone. Bezoars taken from different animals yielded the following amounts of muscone—goat 0.56–0.91, ibex 0.76, chamois 0.38, giraffe 0.17, antelope 0.86, and stag 0.74%.

The anti-bacterial action of eugenol and oil of cloves has been investigated by Bartels,<sup>66</sup> who found that micro-organisms varied in their susceptibility. *E. typhi* and *Monilia albicans* were the most susceptible, whereas *B. pyocyaneus* was the most resistant. Variation in  $p_H$  had little effect upon anti-bacterial action.

Caryophyllene oxide has been isolated from clove oil by Treibs.<sup>67</sup> It is probably identical with the sesquiterpene oxide of Seidel *et al.* (A. 1944, II, 268). Its progenitor is probably caryophyllene and it may be expected generally to accompany the latter in nature. The author, by oxidation

of  $\beta$ -caryophyllene, obtained a 1:4-diketone, the production of which could not be explained on the basis of the formulae of Simonsen (modified version) or Ruzicka. The side chain has been modified to fit the experimental facts:



Littlejohn<sup>68</sup> has given a useful review of the literature of the caryophyllenes to date.

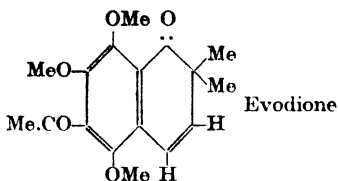
Mitchell and Strausz<sup>69</sup> have prepared citrals by a modification of Tiemann's method (Ber. 1899, 32, 815), from lemongrass oil and from terpeneless lemon oil. An attempt has been made to prepare *isocitral* by Schmidt's process (Schimmel's Ber. 1939, 114) without success, but *isocitral* was obtained by a modified method using sodium methoxide in place of aluminium *isopropoxide*. The lemongrass citral was colourless and had an odour which was slightly harsher than that of the lemon oil citral. The latter product was also colourless whereas the *isocitral* was bright yellow. *isocitral* was rather unstable, but kept well as a 50% solution in absolute alcohol. Its odour was mild but somewhat weaker than that of lemon oil citral. *isocitral* dissolved in an aqueous solution of sodium sulphite and sodium bicarbonate but when regenerated with sodium hydroxide, the product was not *isocitral* but appeared to be identical with ordinary citral. *isocitral*, however, gave a crystalline derivative with sodium bisulphite and could be regenerated unchanged.

*iso*-Pimpinellin, bergaptene and citroptene have been isolated by extraction with ether from air-dried leaves of *Citrus acida*.<sup>70</sup>

The preparation of cyclamen aldehyde,  $p\text{-C}_6\text{H}_4\text{Pr}_3\text{CH}_2\text{CHMe}\cdot\text{CHO}$ , is discussed by Naves.<sup>71</sup> It may be hydrogenated in the presence of Raney nickel to cyclamen alcohol, the acetate of which is hydrogenated to the hexahydro-derivative, hydrolysed to the *cis*hexahydro-alcohol.

*p*-Cymene has been obtained by Sondhi *et al.*<sup>72</sup> in a yield of 30.9% by vapour phase pyrolysis of crude terpineol at 500–515° C. over partially dehydrated gypsum and subsequent treatment with cold conc.  $\text{H}_2\text{SO}_4$ . Vapour phase hydrogenation of crude *p*-cymene over nickel catalyst gave pure *p*-menthane.

Further investigation of evodione,<sup>73</sup> a colourless crystalline ketone isolated from the volatile oil of *Evodia elleryana* indicate it to be 5:7:8-trimethoxy-6-acetyl-2:2-dimethyl-1:2-benzpyran. The evidence of degradation experiments is supported by ultra-violet absorption spectra data.



A review of the fenchenes is given by Littlejohn,<sup>74</sup> including the preparation, characters, identification, constitution, and synthesis of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ -fenchenes with special reference to a new isomer described by W. Hüchel (Ber. 1947, **80**, 197)  $\zeta$ -fenchene.

The dextro-rotatory fraction of an oil obtained from plants of *Mentha piperita* var. *vulgaris* S., grown in southern Ontario,<sup>75</sup> was treated chemically to remove menthone and menthol. It was found impossible to separate pure menthofuran (tetrahydro-4 : 5 : 6 : 7-dimethyl-3 : 5-coumarane) but the purest fraction obtained had a rotation of  $+61^\circ$  and exhibited the properties of this substance. Since menthofuran is present in relatively large quantities in the oil of flowering heads and only traces in oil from the whole plant, it is probable that the source of menthofuran is the flower of the plant.

A synthesis of Civetone and ( $\pm$ )-muscone has been worked out by Blomquist *et al.*<sup>76</sup> Using aleuritic acid as the starting point, 9-octadecene-1 : 18-dioic acid was prepared. The crude acid chloride derived from this was cyclicized through the bi-functional ketene and civetone was obtained in 33% yield. ( $\pm$ )-Muscone was obtained in 22% yield from 14-bromo-3-methyltetradecanoic acid by conversion to 3-methyl-1 : 16-hexadecanedioic acid and the corresponding acid chloride cyclicised through the bi-functional ketene. Muscone (3-methyl-cyclopentadecanone) has been synthesised by Stoll and Rouvé<sup>77</sup> in six steps from sebacic acid : (1) esterification, (2) catalytic reduction to decanediol, (3) bromination to decamethylene dibromide, (4) reaction with acetoacetic ester followed by hydrolysis to dodecamethylene dimethyl diketone, (5) reaction with methyl aniline magnesium bromide, followed by hydrolysis to muscenone, (6) catalytic reduction to muscone.

Nerolidol and Farnesol continue to receive the attention of Naves,<sup>78,79,80</sup> who, in a review of the literature on these two dihydro-sesquiterpene alcohols includes a description of the common adulterants and inferior substitutes. It is pointed out that while nerolidol extracted from oils of the *Myrtaceae* or *Sophoreae* can be readily distinguished from the inferior synthetic product, farnesol synthesised from geranyl acetone is identical with that obtained by isomerisation of natural nerolidol. The author shows that the (+)-nerolidol in Peru Balsam is at least only partly the result of pathological processes since, together with a small amount of farnesol, it constitutes 65% of the acetone-extract of the wood of *Myroxylon pereirae* and 80% of *Myrocarpus fastigiatus* and *M. frondosus* (cabreuva). Carrying this work still further, oils distilled from wood of a healthy tree of *Myroxylon pereirae* and from a tree which had been used for the production of balsam were examined with the following results.

	Healthy tree.	Used tree.
Yield of oil .. ..	0.736%	1.08%
Composition :		
Cadinenes .. ..	28-30%	6-8%
Nerolidol .. ..	50-52%	68-70%
Cadinol .. ..	12-14%	7-9%
Esters .. ..	About 2%	About 6%

Ruzicka *et al.*<sup>81</sup> during an examination of Ambergris have obtained from the mother-liquors of the isolation of ambrein some ketonic material containing dihydro- $\gamma$ -ionone. This same ketone was also prepared by the oxidative degradation of ambrein.<sup>82</sup>

The work which led to the synthesis of irone so ably achieved by two separate groups of workers last year, H. Schinz, L. Ruzicka *et al.* and Y. R. Naves *et al.* is reviewed by Moncrieff.<sup>83</sup> The constitution of irone and the synthesis of ( $\pm$ )- $\alpha$ -irone are also described in detail by a member of one of the teams, H. Schinz.<sup>84</sup>

A new method for the production of ( $\pm$ )-menthol is described by Brode and van Dolah.<sup>85</sup> This is based on the discovery that a mixture of isomeric menthols richer in the desired ( $\pm$ )-menthol is obtained by copper chromite rather than by nickel catalysed hydrogenation of thymol.

## Analytical

The proposed methods of the Brazilian Standards Association for the analysis of essential oils are described and discussed by Littlejohn.<sup>86</sup> It is the author's view that, although the methods are of interest, in that they give details of how the Brazilians assess their oils, they do not compare favourably with the methods adopted in this country.

A number of new specifications have been published during the year by the American Essential Oil Association.<sup>87</sup> In each case, in addition to the solubility in alcohol a statement is made as to the solubility or otherwise of the oil or isolate in benzyl benzoate, mineral oils, fixed oils, diethyl phthalate, propylene glycol, and glycerin. The articles covered by the specifications are oils of copaiba, Ceylon citronella, Java citronella, and ginger; geranyl acetate, citral, geraniol, and citronellol.

The British Aromatic Compound Manufacturers' Association has issued a recommendation to its members to use the hydroxylamine test as a standard method for the determination of citral in lemongrass oil. The views of a number of analytical and consulting chemists were sought, by a London journal, upon this recommendation.<sup>88</sup> Dr. G. W. Ferguson, Mr. C. E. Sage, and Messrs. Salamon and Seaber were all in agreement that the method was to be preferred but was more difficult for suppliers abroad to carry out. These suppliers have been using the bisulphite absorption test for many years, and in view of its simplicity it was felt that it would be very difficult to persuade them to change to a more complicated and lengthy method. Following this recommendation a modification of the published hydroxylamine method has been suggested<sup>89</sup> in that 1 ml. of the oil be pipetted instead of weighing 1 gm. and that the average weight of 0.9 gm. be used in the calculation.

Naves<sup>90</sup> has devised a method for the determination of alcohols in essential oils, by acetylation in the presence of pyridine. It was found

that primary alcohols reacted practically 100%, secondary alcohols 97-93% or less and tertiary alcohols but little.

The methods hitherto proposed for the determination of ascaridol in chenopodium oil have been reviewed by Halpern,<sup>91</sup> and the possibility of using the oxidative property of ascaridol on ascorbic acid has been investigated without success. The need for further investigation of this problem is emphasised.

A method for rapid colorimetric determination of cedrene and cedrol in the air of cedarwood chests is described.<sup>92</sup> This is based on a red-violet colour formation resulting from the reaction of cedrene with vanillin in the presence of HCl. The cedrol is dehydrated by phosphoric acid and determined as cedrene.

An approach towards distinguishing between genuine and adulterated petitgrain and neroli oils has been made by Naves.<sup>93</sup> While neroli oil is still produced by the old method of distillation with a high proportion of water the hydrolysis of the esters is considerable; on the other hand petitgrain is distilled by direct steam, resulting in oils of high ester content. Examination of a petitgrain oil so prepared and also of orange blossom oil distilled from concrete showed that the free linalool was almost entirely optically inactive.  $\alpha$ -Terpineol was present while geraniol and nerol were almost entirely lacking. Esters of terpineol were present in only small proportion. Commercial oils were found to contain optically active linalool increasing in direct proportion to the decrease in ester content. Free geraniol and nerol were present. The esterified linalool was largely *laevo*-rotatory. Examination of the free alcohols will indicate whether alcohols of foreign origin have been added. The alcohols obtained by saponification of the oil will show any addition of synthetic linalyl or terpinyl acetates.

Tetrabromides of  $(-)-\beta$ -phellandrene and other terpenes have been prepared by Berry and Macbeth,<sup>94</sup> and their characters determined. By means of these derivatives the authors were able to differentiate between  $(-)-\beta$ -phellandrene of *Eucalyptus cneorifolia* or Canada balsam and  $(+)-\beta$ -phellandrene from water-fennel oil. Characters are also given for the tetrabromides of  $(\pm)-\beta$ -phellandrene,  $(+)$ -limonene, dipentene, and *p*-mentha-2 : 8(9)-diene (from chenopodium oil).

A cryoscopic method employing congealing temperatures has been developed for the determination of safrole in Brazilian "sassafras" oil and in safrole drainings.<sup>95</sup>

Naves<sup>96</sup> states that while for many years a rhodinol (citronellol) content of between 25 and 40% was accepted as the standard for a genuine Bulgarian otto of rose, subsequent work showed that oils distilled by modern methods contained between 45 and 55% and occasionally up to 63%. The author considers that the old method of adulteration with palmarosa oil may have been replaced by the use of mixtures rich in rhodinol. Since otto of rose contains  $(-)$ -rhodinol with  $\alpha_D - 4$  to  $-4.50^\circ$  and it is not possible to obtain such a product economically from any other source, then adulteration with rhodinol from geranium or other oils will depress the rotatory power of the isolated rhodinol. A method for the isolation of this constituent is described.

A number of workers have reported upon the determination of essential

oils in citrus peels and juices. Deshusses<sup>97</sup> found the Zäch method to give low results on spices, due to evaporation of the oils during treatment with chromic acid, but the amount of oil in lemon and orange peels was determined satisfactorily. Burdick and Allen<sup>98</sup> describe a rapid nephelometric method for the determination of oil in citrus juices, employing distillation with steam and acetone and subsequent dilution of the distillate with water. In proposed standards for grades of canned citrus juices two types of apparatus are described and figured for the determination of the recoverable volatile oil which must not exceed certain maximum percentages.<sup>99</sup>

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# PHOTOGRAPHIC MATERIALS AND PROCESSES

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THE photographic industry has again been straining to supply the much increased demands of users, and production has certainly maintained if not surpassed last year's high level. There are indications, however, that the market requirements of some sensitive materials have been met, and the near future may see a gradual conversion from a seller's to a buyer's market. Under present conditions, a great deal of effort must be expended in technological research, whose object is the solving of immediate production problems, and which is seldom published, other than in patent form.

Until the demand in this country for black-and-white film can be adequately met, one cannot expect a considerable production of colour materials; nevertheless, their manufacture on a restricted scale has continued, and the amount of research recorded in this branch indicates that production facilities alone impede an enhanced production of a wider variety of colour films and prints.

In spite of the mass of research work recorded in the photographic field, there seem to have been no spectacular advances, with the exception of nuclear track plates sensitive to particles of minimum ionisation, described in the section headed "Emulsions." These have already led to a marked advance in our knowledge of the structure of the atom. Of the photographic literature published during the year, special mention should be made of "Photographic Theory" by James and Higgins (Chapman and Hall, 1948). This is a most authoritative account of photographic theory presented in a condensed and very readable form. While Mees' "Theory of the Photographic Process" will remain the classical book on the subject for photographic scientists, James and Higgins' book will be better suited to those scientists who apply photography and for whom a brief account of the theory is sufficient.

## Theory of sensitivity and latent-image formation

A new theory of sensitivity and latent-image formation has been put forward by J. W. Mitchell.<sup>1</sup> Although it is still in the tentative stage and rests on premises that have not been independently established, it is of particular interest because, unlike previous theories, it deals with the dependence of sensitivity on emulsion-making conditions and might be of practical value to the emulsion chemist. In the Gurney-Mott picture,<sup>2</sup> which has held the field for the past ten years, the electron freed by light from a halide ion in the silver-halide grain becomes trapped, *e.g.*, at a silver-sulphide "sensitivity speck," and forms a silver atom by virtue of the silver-ion conductivity of the crystal, which is ascribed to silver ions in interstitial positions or lattice positions adjacent to vacant cation sites. (By a repeated motion of adjacent ions, we may regard the

vacant site itself as mobile). Mitchell retains the notion of successive electronic and ionic processes, which has experimental support, but starts from the assumption that the vacant cation sites are accompanied by vacant anion sites rather than interstitial cations (Schottky rather than Frenkel defects). A vacant anion site can form an *F*-centre by capturing an electron. If many *F*-centres came together, thus excluding the halogen from a small region of the crystal, a particle of silver would result. These ideas, originally developed to explain phenomena in alkali-halide crystals, were first applied to latent-image formation by Anastasevich and Frenkel<sup>3</sup> in 1941.

Within a surface layer about  $10^{-6}$  cm. thick, the concentration of vacant anion sites in the crystal would be raised by lowering the *pAg* (i.e., raising the silver-ion or lowering the halide-ion concentration) in the surrounding aqueous medium. During the precipitation and ripening of a photographic emulsion the *pAg* is high and the concentration of vacant anion sites correspondingly low, but during after-ripening the *pAg* is low and the concentration rises. Mitchell supposes that some of these vacancies are converted to *F*-centres by accepting electrons from sulphide ions or other sources. *F*-centres by themselves are assumed to be mobile, diffusion and coagulation being possible only by the motion of additional vacant anion sites to which the *F*-centre electrons can be transferred. Thus, after-ripening yields a distribution of *F*-centres, *F*-centre aggregates and silver particles, which can be stabilised by a final increase of *pAg*. Electrons would be trapped most readily by the large aggregates and metallic specks: halogen atoms would accept electrons most readily from small aggregates, or isolated centres.

The absorption of light by an *F*-centre, to which process the long-wave-length sensitivity tail in non-dye-sensitised emulsions is ascribed, frees its electron, which becomes trapped at a large aggregate and attracts a vacant anion site, thus adding one *F*-centre to the aggregate. Absorption by a halide ion yields an electron and a halogen atom, which become trapped at large and small aggregates respectively. In each case the net effect is a coagulation of pre-existing *F*-centres without any genuine reduction of the crystal to silver and halogen. This process is identified with latent-image formation, at least so far as fast emulsions and small exposures are concerned.

Mitchell's theory has obvious attractions; for instance, it allows one to understand how latent-image specks can be formed inside the emulsion grain. On the other hand, as yet, there is no clear independent evidence for the existence of *F*-centres in silver-halide crystals.

Applying a totally different line of conjecture to the same problems, Anderau<sup>4</sup> has suggested that the co-ordination of silver ions in the grain surface with gelatine or sensitiser groups and the possible change of the resulting complex from the argento to the argenti form may be of importance for the protection of the unexposed grain against development and the formation of the latent image.

Progress has continued in building up a picture of latent-image formation at a less fundamental level. It is supposed that the latent-image silver speck is at first unstable and subject to recombination (cause of low-intensity reciprocity failure) but after reaching a stable size its

growth is limited only by the sluggishness of ionic motion, which causes the silver to form more dispersely with high-intensity exposures and to form inside the grain even though the surface is favoured at lower intensities (cause of high-intensity reciprocity failure). Burton<sup>5</sup> has shown mathematically that a number of effects can be understood on this basis without an appeal to the basic mechanism. Using special emulsions in which only internal specks are formed, Berg and Burton<sup>6</sup> have confirmed the general picture by the double-exposure technique previously applied to the surface image; in contrast to the previous results, no change of latent-image distribution with exposure time was found (as between the sub-surface and deeper regions of the grain), and the subliminal high-intensity failure observed had to be ascribed merely to a change in dispersity. A more striking confirmation comes from Berg,<sup>7</sup> who argues that early in an exposure at very low intensity (where the exposures can be large owing to reciprocity failure), the few grains bearing specks that have reached the stable size should give off halogen which would desensitise the remaining grains. Using exposure times ranging from hours to weeks, he found a number of effects assignable to this "new cause of low-intensity reciprocity failure." White bands one or two millimetres wide were found in areas of exposed developed film along edges adjacent to areas previously exposed. They were inhibited by treatment with a halogen acceptor, and seemed to mark the zone of diffusion of the photolytic halogen.

Burton<sup>8</sup> reports that latent-image growth and the regression of the hypersensitising effect of a pre-exposure are essentially similar for the surface and internal images. He found also that the Clayden effect still occurs if heat-treatment is substituted for the second exposure: apparently the internal image formed by the intense light flash inhibits the fogging action (surface-image formation) of heat. This suggests that incubation fog is not formed by a local surface reaction but involves the motion of electrons or ions through the crystal. Biltz and Webb<sup>9</sup> have found that the ratio of sensitivities in the natural and dye-sensitised spectral regions is almost independent of exposure time and development time, which confirms that the mechanism of latent-image formation and the resulting latent-image distribution does not depend on the mode of light-absorption.

The Liège workers have continued their investigations of latent-image distribution, solarisation<sup>10,11</sup> and the Herschel effect.<sup>12</sup> Debot<sup>13</sup> has found that the deep internal image, developable after treatment with 5% chromic acid, shows a strong solarisation and second reversal, which in this particular case are due to photochemical reactions occurring in the gelatine: the solarisation is ascribed to tanning of the dichromated gelatine, which impedes development. Sauvenier<sup>14</sup> and Tellez-Plasencia<sup>15</sup> independently report that X-rays yield relatively more internal image than light, but do not take into account the variations of latent-image distribution with light intensity.

The effect of mechanical pressure or friction in forming a latent image has been studied by Mather.<sup>16,17</sup> A strong effect occurs on the concentrated emulsions used for nuclear research though it is largely eliminated by a very thin gelatine supercoat. The effect is put down to intense

local heating. Bäckström *et al.*<sup>18</sup> showed that static pressures up to 3000 atmospheres do not form latent image (in any case this could only occur on applying or relieving the pressure and thus performing work) but produce a reversible lowering of sensitivity, more for high than for low exposing intensities. This suggested that a lowering of ionic conductivity was responsible, which was in fact found to occur.

Pinoir and Pouradier<sup>19</sup> have shown that the effect of supersonic vibrations on photographic films immersed in water is due to luminescence in the water. Banner<sup>20</sup> states that the images produced on a film placed between electrodes across which high-frequency current impulses at 30 *kVp* are passed result from radiation excited in the air-gap rather than conduction in the film.

In a very interesting paper, James, Vanselow, and Quirk<sup>21</sup> describe the use of gold salts as well as mercury vapour for intensifying the latent image. Like post-exposure, gold treatment is more effective for high-intensity exposures, and eliminates high-intensity reciprocity failure. Gold salts and mercury are both effective for post-fixation physical development; the gold salts are best applied after fixation but mercury works only before fixation. Weyerts and Wiederhold<sup>22</sup> have patented a method of "latensification" by sulphur dioxide.

Bullock<sup>23</sup> has studied the changes of sensitivity and developability (physical and chemical) resulting from a partial conversion of the emulsion grains to silver sulphide. The latent image can survive conversion, and it seems that the silver sulphide can appear in two forms according to its mode of preparation, only one form being able to act as a nucleus for development.

Webb<sup>24</sup> has measured the absolute sensitivity of the grains in a thin dilute coating of a low-speed high-contrast emulsion at different wavelengths, finding that about 40 quanta have to be absorbed per grain to make half the grains developable. As is usual in such investigations, the method of arriving at the fraction of light absorbed is the weakest link in the chain.

An article of this kind, covering only the most recent advances, is bound to convey a somewhat disjointed and unbalanced picture of the subject as a whole. This may be corrected by reference to a most comprehensive review of latent-image formation and related matters by Berg,<sup>25</sup> which, together with the present report, brings the subject up-to-date.

## Emulsions

### *Nuclear-particle emulsions*

The use of concentrated photographic emulsions for recording the tracks of nuclear particles continues to grow. Häig<sup>26</sup> gives full details for the preparation of such an emulsion, using acridine orange as a sensitizer, and Cüer<sup>27</sup> has discussed the relevant latent-image questions. The greatest advance in this field has been Berriman's perfection of emulsions capable of recording electron tracks.<sup>28,29</sup> There is evidence that the latest emulsions will record the tracks of any charged particles, however fast, so that no further increase of sensitivity is required.<sup>30</sup>

*Basic emulsion-making materials and processes*

Although gelatine is still the usual binding medium for the sensitive grains, patents on the use of other media continue to appear. New claims refer to hydrophilic polymers of 1:3-dioxalane,<sup>31</sup> hydrophilic hydrolysed interpolymers of a monoolefine and a vinyl ester,<sup>32</sup> and, approaching nearer to the protein configuration, hydrophilic synthetic linear polycarboxamides containing intralinear oxygen atoms.<sup>33</sup> A Japanese paper of 1942 claims that, despite certain drawbacks, whale-skin gelatin can be used instead of the usual beef gelatin.<sup>34</sup>

A revolutionary technique of emulsion-making has been described by Stasiw and Teltow.<sup>35</sup> The silver-halide grains are formed, not by the usual precipitation in gelatin solution, but by "atomising" molten silver bromide with a gas-blast on the scent-spray principle. By adding to the melt 10-30% silver sulphide as a sensitiser and 5% potassium iodide as an anti-foggant, using 95% nitrogen and 5% oxygen in the gas-blast, and annealing the grains before dispersing them in gelatine solution, it is claimed that an emulsion of the highest speed has been prepared (20/10° DIN without optical sensitisation).

Using the conventional methods of making, Sauvenier<sup>36</sup> has studied the influence of the duration of precipitation, ripening, and after-ripening on the X-ray and light sensitivity and contrast of ammoniacal silver-bromide emulsions, mainly with the sort of result one expects from the fact that ripening increases the grain-size while after-ripening confers sensitivity without much change of grain-size: see also <sup>37,38</sup>. In another paper<sup>39</sup> he reports that the internal-image sensitivity increases during ripening but is scarcely affected by after-ripening, which however greatly increases the surface-image sensitivity. Burgers and Kooy<sup>40</sup> have shown that the ripening process can be followed by the increasing resolution of the X-ray diffraction pattern.

*Chemical sensitisers*

Publications on the improvement of emulsions have been concerned less with the basic processes than with the addition of small amounts of various substances, usually during the after-ripening or before coating. *Chemical sensitisers* may be combined on the synergistic principle and judiciously balanced by *anti-foggants* and *stabilisers*, while dyes used as *optical sensitisers* may be enhanced in their effect by colourless *super-sensitisers*. Knowledge of these matters is mostly empirical, and it may not even be clear, for instance, whether a given substance acts as a true sensitiser or merely accelerates development or inhibits the effect of desensitisers present in the gelatine.

Turning first to chemical (*i.e.*, spectrally non-selective) sensitisers, claims have been made concerning the addition to emulsion or developer of certain hydrazine derivatives, *e.g.*, 2-hydrazinobenzthiazole<sup>41</sup>; the addition during after-ripening or incorporation in a separate coating layer of condensation products of aliphatic aldehydes with ammonia or an amine,<sup>42</sup> or certain glycols, saturated aliphatic polyhydric alcohols or their derivatives<sup>43</sup>; and the addition of vitamin B<sub>1</sub> at the beginning of the after-ripening of non-ammoniacal emulsions.<sup>44</sup>

*Retarders, anti-foggants, stabilisers*

Under this heading we include substances (whether present in the gelatine or added deliberately) which retard ripening, restrain fog, stabilise the emulsion against changes of speed and fog after coating, or merely desensitise. The distinction between these actions is not always clear, and the same substance may for instance reduce both speed and fog, so that its use involves a compromise.

Bycichin and Vlach<sup>45</sup> have investigated the ripening of unwashed paper-type ammoniacal silver-bromide emulsions with additions of albumin, lecithin, cystine, and other proteins and their hydrolysis products. Most of these substances retard the growth of speed and fog. The hydrolysis products of gelatine were classified according to their retarding power, cystine having a particularly strong effect. Probably the main effect is a retardation of grain growth. An attempt by Trusov<sup>46</sup> to classify photographic gelatines by their effect on oxygen reduction at a mercury cathode in air-saturated sodium bisulphite solution seems to indicate that surface-active agents in the gelatine also retard the growth of sensitivity during after-ripening.

Bycichin and Vlach<sup>47</sup> describe the use of compounds containing the -SH group as anti-foggants. For instance, mercaptobenzthiazole greatly reduces after-ripening fog in an ammoniacal silver-bromide emulsion, thereby allowing a higher final speed to be attained. A number of patents from Heimbach and co-workers deal with the use of triazaindolinizines as anti-foggants and stabilisers.<sup>48,49,50</sup> Mueller claims that the stabilising and anti-fogging effect of sulphinic or selenic acid is improved by minute additions of cystine, certain substituted cystines,<sup>51</sup> aromatic and heterocyclic polysulphides, or polythionic acids.<sup>52</sup> Trivelli and Smith<sup>53</sup> have patented the addition during or before after-ripening of complex halides of ruthenium, palladium, iridium, or rhodium to offset the fogging action of sulphur-sensitisers.

It is possible that some anti-foggants and the like act by reducing the concentration of free silver ions in the emulsion or by forming protective sheaths around the fog or latent-image nuclei, but Solov'ev and Smirnova<sup>54</sup> have shown that these explanations probably do not apply to the stabilising, or rather desensitising, action of benziminazoles. Comparing various benziminazoles, they find that the desensitising action does not agree with the combining power for silver ions or adsorbability on silver, but there is some evidence that adsorption on to silver bromide is the essential step.

*Anti-bronzing agents*

Photographic papers sometimes show a troublesome phenomenon known as bronzing. This consists of a change of image-colour and reduction of density when a developed, fixed, and washed image is subjected to a high temperature, as in hot-drum drying. Although little is known as to the mechanism of bronzing, many substances have been found to reduce or eliminate it when added to the emulsion or processing baths; as in the anti-foggants and stabilisers, mercapto groups and azoles are prominent here. One might hazard the guess that bronzing represents a recrystallisation of the filamentary developed silver, which anti-bronzers

prevent by becoming adsorbed to faces of the silver crystals, or by reducing the concentration of silver ions or atoms in the mobile phase.

Kendall and Fry<sup>55</sup> claim that a concentration of the order  $10^{-4}$  of a mercapto-1 : 3 : 4-thiadiazole or similar compound in the emulsion or an adjacent layer or the processing solution alleviates bronzing. Dimsdale and Robinson claim advantages for the compounds of azoles with silver or other metals of groups Ib and VIII,<sup>56,57</sup> which retain the anti-bronzing action without the considerable loss of speed caused by the parent compound. The effect of treating the compound with silver ions is probably the same as that observed by Solov'ev and Smirnova<sup>54</sup> in another connection : the desensitising action of certain benziminazoles could be counteracted by subsequent treatment with silver nitrate.

### *Optical sensitisation*

Continuing their studies on the fundamental aspects of optical sensitisation, Solov'ev and his co-workers in Moscow have turned their attention from the developed image to the direct photolytic production of silver. Dealing first with pure silver bromide, not sensitised by a dye, Yampol'skii and Solov'ev<sup>58</sup> made a valuable study of the long-known but little-understood extension of photolytic sensitivity to long wavelengths caused by the presence of photolytic silver, without, however, throwing fresh light on the mechanism of the process, which may or may not be the same as that involved in dye-sensitisation. The quantum efficiency for the production of new silver by this process was found to be 0.07 at a wave-length of  $546\text{ m}\mu$  and 0.05 at  $578\text{ m}\mu$ . As the exposure proceeded, the rate of formation of silver at first rose autocatalytically—in contrast to the initially constant rate observed with blue light—but soon became constant. At the same time, the visual darkening reached a saturation value. This can be understood if the light is absorbed mainly by particles of a given size and the formation of silver ultimately proceeds by an increase in size rather than number of particles. The main conclusion from this work was a practical one : that the absorption of light by the silver could be neglected in the presence of a sensitising dye, provided that the ratio of silver to silver bromide did not exceed 1 : 5000.

In a subsequent paper,<sup>59</sup> the authors give measurements of quantum efficiency for the production of silver by light of wave-lengths 436, 546, and  $578\text{ m}\mu$  acting on suspensions of silver bromide in sodium nitrite solution (a halogen acceptor) with the addition of various dyes, which absorbed only at the longer wave-lengths. At  $436\text{ m}\mu$ , values ranging from 0.7 to 1.0 were found ; in the dye-sensitised region, values from 0.04 to 0.21. A striking result was that for a given dye the quantum yield varied between 546 and  $578\text{ m}\mu$ , being greater for the wave-length lying nearer to the sensitising maximum. One is tempted to regard this as a secondary effect, arising perhaps from the presence of the dye in two or more states of adsorption or aggregation having different wave-length-independent sensitising efficiencies. It should be recalled that previous workers have found quantum efficiencies of about 1.0 for dye-sensitised photolysis and, for the developed image, equal efficiencies in the regions of silver-bromide and dye absorption.

Many years ago Lescynski<sup>60</sup> and Tollert<sup>61</sup> found that the absorption

of light (550  $m\mu$ ) by erythrosin used as a sensitising dye yielded up to 60 photolytic silver atoms per dye molecule, showing that the dye molecule can repeatedly absorb light and give rise to the reaction,  $AgBr \rightarrow Ag + Br$ , without being destroyed. Eggert, Meidinger, and Arens<sup>62</sup> have now confirmed this result under more extreme conditions, namely with polymethine dyes of high molecular weight ( $\sim 550$ ) that sensitise in the infra-red. In particular, up to 160 silver atoms per dye molecule were produced in an emulsion exposed at 950  $m\mu$ .

Putseiko<sup>63</sup> has found agreement of the spectral absorption and photo-electric effect for a number of sensitising dyes, the latter effect being measured as the change in capacity of a condenser filled with the dye. The exciting light passed through a semi-transparent electrode forming one plate of the condenser. A positive voltage on this electrode enhanced the effect in the case of phthalocyanine, and this was interpreted as indicating a positive-hole mechanism of conduction.

The question of chemical desensitisation by optical sensitisers has been greatly clarified in a paper by Spence and Carroll.<sup>64</sup> They regard the sensitising action of a dye as the resultant of three properties, (i) its capacity for absorbing light, (ii) its efficiency in transferring the energy to the silver halide, and (iii) its tendency to desensitise, of which only the absorption is spectrally selective; each of these properties seems to vary independently from dye to dye. As is well known, as the concentration of dye is increased the conferred sensitivity at first rises in proportion to the absorption of the dye, but later reaches a maximum and falls again. In a purely formal sense one may say that the optical sensitisation follows the absorption but is offset by a desensitisation increasing at first less rapidly, then more rapidly than the absorption. The crucial point made by Spence and Carroll is that this formal desensitisation turns out to be substantially equal to the desensitisation that actually occurs at a wave-length where only the silver halide absorbs (400  $m\mu$ ). In other words, the quantum efficiency in the dye-sensitised region relative to that at 400  $m\mu$ , measured as the ratio of the absorbed energies at 400  $m\mu$  and at the sensitisation peak needed to produce a certain developed density, did not vary significantly with dye concentration. This ratio, which was about 0.05 for one dye and 0.9 for another, they interpret as the efficiency of energy transfer. A theoretical and a practical conclusion emerge from this work. Firstly, optical sensitisation affects only the primary photo-electric step in latent-image formation, while the desensitisation (as had previously been found with strong desensitisers such as phenosafranin) comes into play only at a later stage. Secondly, even with the best dyes an appreciable desensitisation occurs, which, balanced against absorption, determines the optimal dye concentration. Spence and Carroll regard the earlier finding that the optimal concentration roughly corresponded to a monomolecular adsorbed layer as merely coincidental.

A few papers on the state of aggregation of sensitising dyes have appeared. Dickinson<sup>65</sup> has compared solutions of 1-methyl-1'-ethyl-2:2'-cyanine chloride and isoquinoline red chloride, dyes having a planar and a non-planar molecular structure respectively, with regard to their light absorption, sensitisation, osmotic pressure, and electrical

conductivity. The two last-named properties indicate that the first dye is aggregated or polymerised; it gives a sharp peak of sensitivity at  $572\text{ m}\mu$ , falling off sharply towards longer wave-lengths. The second dye is monomeric and gives a broad sensitising band. This supports the view that planarity favours polymerisation and polymerisation favours "peak" sensitising. In another paper on aggregation and sensitisation<sup>66</sup> he shows that certain dyes can be adsorbed to silver bromide in three different states of aggregation. Because some dyes may sensitise in the form of crystal-like aggregates, Solov'ev and Yampolskii<sup>67</sup> have examined the reflection coefficients ( $R$ ) of dye crystals spread on glass,  $1/R$  having previously been found to vary with wave-length in the same way as the absorption. In some cases an agreement with the sensitising effect was found; for instance, erythrosin has a maximum of  $1/R$  at  $572\text{ m}\mu$  corresponding to the sensitivity peak in emulsions containing much erythrosin, as well as the  $525\text{ m}\mu$  peak found in the absorption of aqueous solutions.

#### *New optically sensitising dyes*

Reports on new dyes for optical sensitisation are of rather limited interest; they occupy more space in the literature than the more general studies discussed above, but less in the present review. Progress has continued in the interesting field of trinuclear cyanine dyes, which appear as by-products in the preparation of carbocyanines: Hamer, Rathbone, and Winton<sup>68</sup> deal with the synthesis of neocyanines, Anish<sup>69</sup> describes a new class of dyes in which the third nucleus is joined to the monomethine chain between the other two without interrupting the linkage and two nitrogen atoms are quaternised instead of only one as in the usual cyanines, and Riester<sup>70</sup> describes types in which the three nuclei are joined linearly, Wilson<sup>71</sup> describes the preparation of some polymeric cyanine dyes and intermediates. Cyanine dyes of various types having alkyl or more complicated groups as substituents in the chain are described by Hamer and Knott,<sup>72</sup> Anish,<sup>73</sup> and Kendall<sup>74</sup>; Brooker and Keyes<sup>75</sup> claim as sensitisers carbocyanine and merocyanine dyes containing cycloalkyl substituents; Anish<sup>76</sup> described benzoxacarbocyanines having branched chains on the benzene rings. An interesting variant occurs in sensitising dyes prepared by Brooker<sup>77</sup> from *N*-arylthiazolinium quaternary salts; the usual cyanine dyes have alkyl groups attached to the nitrogen atoms, but these have aryl. Among other patents may be mentioned one by Riester and Wilmanns.<sup>78</sup> Sensitisers are prepared by the reaction of dyes containing thiohydantoin nuclei with, *e.g.*, alkyl halides followed by condensation with nitrogenous heterocyclic compounds having reactive methyl or methylene groups. These are claimed to be intense, and suitable for colour photography because they are stable against reaction with colour formers and do not diffuse. A physical property is also stressed in patents by Heimbach<sup>79</sup> on asymmetrical 1-, 3-, 4-triazaindolizine cyanine sensitising dyes, which are water-soluble and thus, for instance, can be readily removed during processing.

#### *Supersensitisers*

Supersensitisation is said to occur when the optical sensitisation produced by a combination of substances exceeds the sum of their separate

effects. In some cases one can distinguish the main sensitising dye from the auxiliary supersensitiser, the later being colourless or present in low concentration. Supersensitisation may or may not be spectrally selective; it is known to increase the primary step, the transfer of energy from dye to crystal, but whether it does this by altering the physical state of the dye or in some more subtle way is uncertain.

A patent by Carroll, Brooker, and Spence<sup>80</sup> on the superadditive sensitisation of certain acid and basic dyes taken in pairs seems to contain a hint that mutually-assisted adsorption may be playing a significant rôle. Nicholson and Collins<sup>81</sup> describe the use of 9-alkyl-thiacarbo-cyanines in concentrations too low to sensitise directly as supersensitisers for oxa-, thia-, or seleno-pseudocyanine dyes. Turning to colourless substances, Fallesen and Leermakers<sup>82</sup> describe the use, with similar dyes, of esters of the type  $R'CO_2R''$  where  $R'$  and  $R''$  are alkyl, aralkyl, or aryl, while Carroll and Spence describe a number of substances—ketones,<sup>83</sup> aldehydes,<sup>84</sup> heterocyclic nitrogen bases such as 2-quinoline,<sup>85</sup> and aryl cyanides having no acid groups, such as  $PhCN$ <sup>86</sup>—which are said to favour particularly the "second peak" of sensitisation which appears at high dye-concentrations.

#### *Contrast-lowering dyes*

Davey and Knott<sup>87</sup> have patented the incorporation of a benzylidene-pyruvic acid together with nitro-aniline or nitro-anilinesulphonic acid in the emulsion. These substances increase the light absorption (without optical sensitisation) in the near ultra-violet and thus lower the contrast, enabling a more uniform contrast to be obtained throughout the near and far ultra-violet.

#### **Film support**

Special mention should be made of a most comprehensive paper by Calhoun<sup>88</sup> on the chemical and physical properties of film bases, which can be regarded as a valuable addition to photographic literature. The discussion is mainly from the point of view of dimensional stability, and changes of dimension with humidity and temperature on processing and on storage are quantitatively described. Quantitative data are also given on the effect of temperature and humidity on the physical characteristics of the film base, such as tensile strength, elongation, brittleness, etc.

#### **Processing**

An important contribution to our knowledge of the mechanism of development has been made by G. I. P. Levenson,<sup>89</sup> who has studied the separate and combined effects of N-methyl *p*-aminophenol sulphate (elon or metol) and hydroquinone. A combination of elon and hydroquinone shows "superadditivity," *i.e.*, their combined effect in terms of the rate of reduction of silver bromide is greater than would be expected from their separate activities. By oxidation and analysis of developers under various conditions, Levenson showed that even under conditions when hydroquinone alone would have a negligible developing effect, it

can assist actively in the combined developer by regenerating elon from its oxidised form, presumably the methyl quinonimine. A comparison of the development characteristics of *p*-aminophenol and *N*-methyl *p*-aminophenol was made by Shishkina,<sup>90</sup> who found equal velocities of development when the  $p_H$ 's of the two solutions were adjusted to give the same "redox" potential. It should be pointed out that, strictly speaking, it is improper to refer to the "redox" potential of a developer, since reduction-oxidation potential refers to conditions of thermodynamic equilibrium in a reversible system, whereas in development, the sulphite removes the oxidised developer by an irreversible sulphonation. However, the term is commonly used, since under suitable experimental conditions, reproducible potentials are assumed by a bright platinum electrode in developer solutions. Shishkina found that on varying the  $p_H$ , the velocity of development was in each case a linear function of the "redox" potential. Bürki and Jenny<sup>91</sup> confirmed this relation, but only over a limited region, for catechol, hydroquinone, *o*- and *p*-phenylenediamine, pyrogallol, *p*-aminophenol, *p*-hydroxyphenylglycine, elon, and elon-hydroquinone developers.

Mott<sup>92</sup> has replied to criticisms of the electrolytic reduction mechanism of development postulated in the Gurney-Mott theory.

No significant advances have been made in the general practice of processing, though Bean<sup>93</sup> claims to have solved the problem of making a ready-mixed dry packed developer which is stable and non-caking. The difficulty lies in obtaining air-stable, moisture-resistant alkalis, and Bean proposes the use of the disodium salts of monohydroxyphenol, monocarboxylic or sulphonic acids. The activity of a developer containing a phenol carboxylate is the same as that containing an equimolecular weight of sodium hydroxide, though the sulphonates are less alkaline. Bates<sup>94</sup> finds that the inclusion of a thallium salt in a developer gives higher speed and contrast, especially with emulsions of high iodine content, and Stevens<sup>95</sup> has described a development technique for nuclear-track plates, which will distinguish fission fragment tracks from alpha particle tracks. A valuable paper on the identification, formation, prevention, and removal of scums, sludges, and stains which may occur on sensitive material during processing has been published by Crabtree and Henn<sup>96</sup> following their comprehensive paper on sulphide stain,<sup>97</sup> and Crandall<sup>98</sup> has investigated the removal and prevention of fungus stain on photographic negatives in the tropics. The blue stain caused by fungus mycelium may be removed by a normal hypo bath, and bacterial growths on newly processed film are prevented by a dip in 0.1% mercuric chloride, or 0.24% Lignasan. One of the difficulties of cold glazing of prints by squeegeeing and drying on glass is the proper conditioning of the glass surface, and Gerould and Woodland<sup>99</sup> describe the preparation of improved glass surfaces for this purpose by forming organo-siloxanes thereon. The specular deposit of silver which may form on the surface of a sensitive material under abnormal development conditions has been investigated by Plotnikov,<sup>100</sup> who gives optimal conditions for such silvering.

Work on high-speed processing has continued, and Burkin<sup>101</sup> has described methods of processing prehardened films in 6-15 secs., and

ordinary film in 30 secs. The usual methods of high temperature development in highly alkaline elon-hydroquinone, and high temperature fixation in ammonium thiocyanate were employed. A number of papers have appeared dealing with combined developer-fixing baths. Keller, Maetzig, and Möglich<sup>102</sup> counteract the unreliability and the adverse effect on speed of such baths by using as  $p_H$  buffers sodium plumbite, zincate or aluminate, the latter also acting as a hardening agent. Safranine was suggested as a developer accelerator, and benziminazole was shown to be preferable to bromide as an anti-foggant, provided that the developer-fixer is used in a fresh condition. Hypo was found by Miller and Crabtree<sup>103</sup> to be preferable to ammonium thiosulphate, alkali thiocyanate, ethylenediamine, potassium cyanide, or morpholine when used as the fixing constituent of a developer-fixer. A one-bath developer-fixer giving a complete range of image tones is described by Carrell,<sup>104</sup> who uses thiourea physical development. The range of tones is obtained by varying the development times and the proportions of the three main constituents of the solution, which are (a) silver nitrate-sodium sulphite-hypo, (b) elon-hydroquinone-carbonate, and (c) thiourea-ammonium bromide. The main application of the technique is in the production of warm-tone lantern plates. A one-bath reversal process has been described by Miller.<sup>105</sup> After suitable treatment in a hypo-containing developer, the material is removed and flashed to light. Development and fixation of the remaining silver halide is due to the solution contained in the emulsion layer. Miller shows that the effect is different from the normal Sabattier reversal, as it is, over a wide range, independent of exposure. His experiments lead to the rather surprising conclusion that rate of fixation in the first treatment increases with the amount of silver developed in the immediate neighbourhood. Since the latitude is small, and the reversed image confined to low densities, the application of this interesting technique would appear to be limited, *e.g.*, to the duplication of negatives of low density range. The normal reversal process has been studied by Leistner,<sup>106</sup> who recommends prolonged first development in an energetic non-solvent developer. He suggests the conversion of the negative silver to silver iodide by iodine treatment as an alternative to its removal by acid permanganate.

Reagents for the prevention of fog or bronzing are preferably applied as additions to emulsions (see section on "Emulsions"), but some reagents are more suited to inclusion in the developer. It has been discovered by Fallesen<sup>107</sup> that the presence of aromatic hydrocarbons or their halogen derivatives in developers reduces fog on ultra-sensitive products without undue loss of speed, and Chilton, Kendall, and Phillips<sup>108</sup> have patented the treatment of a developed silver image with substituted 5-mercaptotetrazoles or 5-mercapto-1 : 2 : 4-triazoles for the prevention of bronzing of paper prints.

In the analytical field, Levenson has continued his studies of the analysis of developers, and has published methods for the determination of iodide<sup>109</sup> and of copper<sup>110</sup> therein. A method for the determination of small amounts of silver has been described by Tellez-Plasencia.<sup>111</sup> Excess of 0.001-M alcoholic solution of *p*-dimethylbenzylidenerhodanine is added to the silver solution, and the excess determined colorimetrically.

### New materials and processes

Rott's inversion-transfer method, which is the principle upon which the Land process (see 1947 Report) is based, has been further developed. Rott<sup>112</sup> has described a "contour" film, suitable for the production of outline-images. A film is coated with a hardened unsensitised emulsion containing nuclei suitable for physical development, and super-coated with an unhardened orthochromatic emulsion. On exposure to an original and suitable development, a negative image is obtained in both layers, together with a positive image in the lower layer only, formed by physical development of the excess halide from the upper layer, and when the upper layer is removed, the negative and positive images of the lower layer are distinguished by black, and violet or brown image colours, respectively, giving a contour effect. Exposure to green light gives a positive image only in the lower layer. Dobbins<sup>113</sup> has described a reflex-process for document copying, in which the document is covered with a layer of light-permeable phosphor. The sensitive paper is then placed face-down over the document so that the activated phosphor is sandwiched between the two. Differentiation between the light and dark portions of the document is obtained owing to differences in inter-reflection between the layers as in the normal reflex process.

The Corning photo-sensitive glass has been studied by Riess, Bosch, and Reboul,<sup>114</sup> who prefer development at 540–565° C. instead of the recommended temperature of 630° C., so as to avoid softening the glass. Selényi<sup>115</sup> has investigated the photographic properties of selenium. A selenium mirror was prepared by polishing a deposit of selenium containing 0.07% iodine on a steel or aluminium base, and was found capable of producing a faint image on exposure at 90–95° C., due to light-accelerated crystallisation of the amorphous selenium.

### Colour photography

There are no marked advances to report in the field of colour-photography. Research and development have been directed very largely to the monopack subtractive process, using colour development. Schmidt and Sprung,<sup>116</sup> and also Hanford,<sup>117</sup> have patents relating to aromatic hydrazine derivatives, which form azo dyes with suitable couplers when used as colour developers, and Morreall<sup>118</sup> finds that the speed of the emulsion and the rate of colour development are increased when development is carried out in the presence of urea or an N-substituted urea. The effect of urea is more marked in the lower layers of the emulsion, and is ascribed to its action in modifying swelling characteristics. One of the difficulties of colour development is the production of stain, and Jennings<sup>119</sup> reduces this undesirable and excessive colour formation by introducing during or immediately after colour development, an aldehyde or ketone containing carboxyl, amino, hydroxyl, sulphonyl or other solubilising group. Such a compound reacts with the developing agent or the products of development to form a water-soluble compound which is subsequently washed out during processing. Another method of producing a similar effect is due to Weissberger, Kibler, and Porter,<sup>120</sup> who show that the addition of an acyl group to the reactive methylene

group of the colour-former not only hinders diffusion of the coupler, but also lowers the activity of the coupler and reduces stain. A further improvement in colour processing has been suggested by Edgerton,<sup>121</sup> who finds that the amount of dye removed by an acid dichromate bleach bath is diminished to negligible proportions during normal bleaching times by the inclusion in the bleach bath of a wetting agent.

Judging by the patent literature the bulk of the research and development work in colour photography has been directed towards the discovery of new colour formers designed for use not only with amino developers to give azomethine or quinonimine-dyes, but also with aryl hydrazine developers to give azo-dyes. Bavley<sup>122</sup> finds that the activity of a coupler is increased if the reactive methylene group attached to a heterocyclic coupler is itself part of a second ring structure. Among the new couplers, urethanes derived from N-substituted J. acid,<sup>123</sup> acetyl R-heterocyclic colour formers,<sup>124</sup> heterocyclic groups linked by a methine group,<sup>125</sup> acylacetylmethine derivatives of heterocyclic N-compounds,<sup>126</sup> bipyrazoline derivatives,<sup>127</sup> substituted pyrazolones,<sup>128</sup> aminopyrazolones,<sup>129</sup> diketopyrazolidine derivatives,<sup>130</sup> cyanoacetylaminophenol,<sup>131</sup> naphthol-sulphonamide derivatives,<sup>132</sup> arylpropylene derivatives,<sup>133</sup> condensation products of salicyl aldehyde with primary amines,<sup>134</sup> aracylacetyl derivatives of an alkyl or aryl amide,<sup>135</sup> polymeric quaternary ammonium salts,<sup>136</sup> or their methods of preparation have all appeared in the patent literature.

Jennings<sup>137</sup> has attached the colour-former molecule to the hydrophilic protein used as a vehicle for the silver halide, by means of a bi-functional condensation agent, and in a second patent, Jennings, Murray, and White<sup>138</sup> covers the use of synthetic polymers which act as the silver halide vehicle, and at the same time contain units capable of acting as colour-couplers.

Further modification of the coloured-coupler technique for self-masking described in the 1947 Reports have been patented. The intensity of colour of the original coloured coupler can be matched against the unwanted colour of the final dye by using an appropriate mixture of coloured and uncoloured coupler, both of which give the same dye image on developer coupling (Vittum and Arnold).<sup>139</sup>

Jelley and Vittum<sup>140</sup> describe an ingenious method in which the coupler used is the final dye image which is differentially removed by colour developing and subsequently treating with a strong acid which destroys only the azomethine dye formed during development. This method gives a positive coloured image by negative development only, followed by coupled-dye destruction and removal of developed silver and unchanged silver halide. A further modification due to Vittum, Weissberger, and Wilder<sup>141</sup> describes the incorporation of solubilising groups, so that water washing may be substituted for the acid treatment.

A new method of masking when making colour separation negatives from a transparency has been described by Yule,<sup>142</sup> who makes use of the Clayden effect, *i.e.*, the desensitising of an emulsion by means of a very short duration, high-intensity exposure before the main exposure. In preparing, for example, a green separation negative by exposing pan-film behind a transparency and a green filter, this step is preceded

by a high-intensity, extremely short exposure behind a red filter, producing local de-sensitisation which compensates for the undesirable green absorption of the cyan dye. The method may be adapted to the unsharp mask technique. Harsh and Friedman<sup>143</sup> describe the production of separation negatives in motion picture work by the use of film giving equal contrast under red, green, and blue filters at the same time of development, so that the black and white separations may be obtained on successive frames of a 35 mm. film. Two very similar systems have been described in which the three adjacent emulsion layers are exposed as a bi-pack through one support. In one, the blue and green sensitive emulsions are coated on the front film<sup>144</sup> and in the other, the green and red sensitive layers on the rear support.<sup>145</sup> The two layers on the same support have in each case an intermediate layer which allows transference of the upper emulsion during or after development. Stott<sup>146</sup> has suggested a method for the separate processing of the two sides of a two-colour film by temporarily protecting one side by means of a removable lacquer coating. The use of a monopack consisting of three separate coatings might be avoided, and a single emulsion layer substituted, by successive exposures behind tricolour filters and suitable colour development, except that the sensitivity of the single emulsion is seriously impaired by such pre-treatment. Neumann<sup>147</sup> claims to have overcome this difficulty by treatment between each exposure and development with phthalic anhydride, hexamethylene tetramine, and a soluble halide. An alternative method which not only avoids local differences in sensitivity, but also maintains the amount of available silver halide at a constant level, has been suggested by Hanson and Farrell.<sup>148</sup> After each exposure and colour development, the residual silver halide is flashed and developed in a colour developer which forms a soluble dye image. The whole of the silver in the layer is re-halogenated ready for the next exposure, and the soluble dye removed by washing.

Dye transfer methods have been studied by Bromberg and Maltzeva,<sup>149</sup> who have investigated the effect of variations of such conditions as  $p_{\text{H}}$ , temperature, emulsion thickness, tanning conditions, etc., on the swelling of the emulsion layer. The kinetics of dye imbibition and transfer were also studied. Beal<sup>150</sup> has published a paper on mould growth in dye solution, and tricolour dye solutions have been suggested by Haff.<sup>151</sup>

Of new colour processes, Wright<sup>152</sup> has patented an additive process in which separation into spectral colours is accomplished by the use of polarised light, and a pleochroic substance included in the emulsion layer, and a colour process which could be used for stereoscopic projection has been described by Husek,<sup>153</sup> based on the production of polarising dye images, using Prussian blue as a temporary mordant.

### Photo-mechanical processes

Three papers have appeared dealing with the etching of copper by ferric chloride. In the first, by Slunder and Vaaler,<sup>154</sup> the effect of copper salt concentration on the "redox" potential of ferric chloride solution is studied; in the second paper, Vaaler<sup>155</sup> describes its effect on etching characteristics for both line work and half-tone, and in the third,<sup>156</sup> the same author investigates the effect of free HCl in the etching solution

(i.e., HCl in excess of that produced by hydrolysis of ferric chloride). He recommends that excess HCl should not exceed 0.25% if failure of the fish glue stencil is to be avoided.

The substitution of blood albumin for egg albumin in the dichromated albumin solution used in photo-lithography has been patented by van Dusen,<sup>157</sup> who claims that it is entirely free from liability to contamination by fungus or mould. The corrosion of aluminium plates used in lithography, which occurs in certain regions, due to characteristics of the water supply may be minimised by treatment in an ammonium dichromate-hydrochloric acid solution.<sup>158</sup> A novel method of preparing aluminium off-set printing plates to give durable results has been suggested by Schwarz,<sup>159</sup> and Mullen<sup>160</sup> has described the preparation of photogravure printing plates on a resin-treated paper base. A method of producing a printing image on a transparent plastic base has been devised by Filmer,<sup>161</sup> who applies in succession an opaque lacquer, a dichromated colloid and an orienting pattern which is actinically transparent. The material is exposed, etched, and the uncovered lacquer dissolved, giving an image which can be printed on an off-set machine, or used as a photographic negative. Rice<sup>162</sup> describes a half-tone image in gelatin relief which can be printed by dye imbibition, and Switzer and Switzer<sup>163</sup> patent a method for separating the colours of an original by incorporating suitable fluors in the colours and photographing by ultra-violet.

### Diazo and blue-print processes

The diazo process continues to attract the attention of research workers. Perhaps the most interesting papers are those describing a new light-sensitive system (Dippel and Keuning<sup>164</sup>; Alink, Dippel, and Keuning<sup>165</sup>) in which a combination of a diazonium salt and a metal salt (e.g., mercurous nitrate) gives on exposure to light a latent image of the metal which can be physically developed to give an image of metallic silver. The light sensitivity of the system is several times that of the normal diazo type papers, and high gamma (6-8) and resolving power (more than 1000 lines/mm.) are claimed. The authors recommend the process for the reproduction of documents and of sound tracks. The main object of research on the diazo process seems to be the stabilising of diazo papers, and Chechak<sup>166</sup> has found that the diazobiguanides are more stable than the diazonium salts themselves. A number of patents have been granted covering new azo couplers, for which high visual density of image, and stability of the paper are claimed. Instead of the usual azo couplers, such as phloroglucinol, or resorcinol, the following have been patented: (a) the molecular compound of phloroglucinol with a tertiary amine,<sup>167</sup> (b) resorcinol monoesters,<sup>168</sup> (c) phloroglucide,<sup>169</sup> (d) thiourea derivatives of phenols,<sup>170</sup> and (e) hydroxypyridones.<sup>171</sup> Slifkin<sup>172</sup> finds that a diazo-type paper is stabilised by the presence of orthophosphoric acid and a weak organic acid, while von Glahn and Reichel<sup>173</sup> patent the substitution for sodium bisulphite as stabiliser, of the bisulphite compound of ketones or aldehydes.

For the improvement of blueprint material, Jahoda<sup>174</sup> has suggested pre-coating the sized paper base with a silica sol, which, he claims, prevents the passage into the base of colloidal materials in the ferric

coating, and gives a wider speed range and more intense blues. Vallen and van der Dolder<sup>175</sup> find that a pre-coat with sodium fluoride gives improved keeping properties.

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# SANITATION AND WATER PURIFICATION

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## Water

### *Gathering grounds*

AN important event during the year was the publication, by a Sub-Committee of the Central Advisory Water Committee, of a report containing its conclusions on the protection of gathering grounds for public water supplies. The Committee recommends that sewage and drainage from farmyard manure should be prevented from draining into reservoirs or into streams which feed them. Gathering grounds, however, may be used for agricultural purposes or may be afforested; the general public may have access to them, though not to the banks of reservoirs, which should not be used for bathing, though they may be used for fishing and boating with strict safeguards.<sup>1</sup>

Bacteriological conditions in a reservoir in the Tennessee Valley have been studied by Clark and Kittrell<sup>2</sup>; the reservoir is, at present, polluted by sewage and the authors discuss the extent to which these discharges would have to be treated to bring the concentration of bacteria in the reservoir below a given value at different temperatures. The numbers of coliform organisms in the reservoir increased significantly on days when the rainfall exceeded 0.6 in.; similar observations have been made by other workers, but comparatively little is yet known about the general relation between intensity and duration of rainfall, type of land drained, and numbers and types of bacteria in the surface waters.

### *Coagulation and filtration*

Few advances in methods of removing suspended and colloidal matter from water have been reported during the year. The use of "activated silica" is becoming widespread in America; according to Merrill<sup>3</sup> the substances now used in conjunction with sodium silicate are mainly sulphuric acid or ammonium sulphate, though many others have been tried.

Interest is still being maintained in the various processes of forming coagulants by passing an electric current between plates of the metal. In some of the earlier plants the whole of the water to be treated flowed through the electrolytic cell, but it is now more usual to pass only part of the water through the cell; this water, containing a relatively strong solution of the metallic salt, is then mixed with the bulk of the water to be treated.<sup>4</sup>

There is an interesting description of a flocculator with no moving parts. Water, to which a coagulant has been added, is passed through a straight channel fitted with baffles and designed so that the velocity decreases from the inlet to the outlet end. In one plant of this type

the loss of head is about 18 in. and the period of retention about 30 minutes.<sup>5</sup>

Results of a year's experience with a micro-straining plant have been given by Hornby and Thomas.<sup>6</sup> One difficulty encountered in the early stages was the accumulation of air between the screening fabric and the supporting metallic drum, which was originally made of stainless steel; this has been eliminated by using a cylinder of Monel metal, which is more easily wettable than stainless steel. The volume of water used for washing the strainers is about 1.1% of the total volume treated. After straining, the water is treated in sand-filters; the preliminary straining has increased the capacity of these by about 15%. A paper by Key<sup>7</sup>—of which only a long abstract is available—describes experiments in which the effect of air scour was observed in a model sand filter of which one side was of glass. In general, air scour had little effect on the cleaning of the bed during backwashing; bubbles of air remained in the bottom gravel and silt was carried upwards only near the waste water troughs, where the upward velocity of the backwash water is greatest. As a result of this work Key designed a filter in which the upward velocity of the backwash water would be more uniform over the whole cross-section of the filter.

### *Bacteria*

An important advance has been made by Mackenzie and others<sup>8</sup> in the determination of coliform bacteria in water. Two tubes, one containing brilliant green bile broth and the other peptone water, are inoculated from a MacConkey broth tube which has given a positive reaction. Both tubes are incubated for 24 hours at 44° after which the brilliant green bile broth tube is examined for production of gas and the peptone water is tested for indole. A positive result from each test indicates *B. coli*, type I, the tests differentiating this organism from Irregular types II and VI. By this method an examination can be made in two days, as against five days for the plating method. The iron bacteria have been studied by Duchon and Miller,<sup>9</sup> who give data on their nutritional requirements, isolation, and response to a wide range of bactericidal substances. Clegg and Sherwood<sup>10</sup> have described the enumeration of coliform bacteria in molluscan shellfish by various methods, of which the "roll-tube" method is the most satisfactory. From America there is an extremely interesting account of the effect of sulphate pulp mill wastes on oysters in the York River.<sup>11</sup> Although these wastes are not produced on any large scale in Great Britain the methods used in the work, particularly those used to study quantitatively the reaction of oysters to toxic substances, are of wide application.

### *Disinfection*

Although chlorine is so extensively used for disinfection of water there has hitherto been very little quantitative information on its effect, in the various forms in which it may be present in aqueous solution, on different species of bacteria. Two important papers on this subject have been published during the year. Fair and others<sup>12</sup> give data for the relative sterilising effects of HOCl and OCl' and show that their toxicities

to *Eberthella histolytica* are additive. Similarly, the sterilising effects of monochloramine and dichloramine are additive. Butterfield<sup>13</sup> summarises a great deal of work carried out by the United States Public Health Service on the bactericidal properties of chloramine and free chlorine on pure cultures of bacteria, including some pathogenic species. The minimum concentration of chloramine required to effect a given reduction in bacterial count is much higher than that of chlorine; to obtain a 100% kill with a given concentration of residual chloramine required a period of contact approximately 100 times as long as with the same concentration of free chlorine. It is reported<sup>14</sup> that chlorine dioxide is now being used in some 65 towns in U.S.A. and in about 15 in Canada; the chief use is to destroy organic matter in water so as to reduce the quantity of chlorine necessary to kill bacteria. Palin<sup>15</sup> has confirmed that chlorine dioxide does not react with ammonia, the relation between amount added to a water and residual concentration being linear. He has shown that taste due to chlorophenols can be destroyed by addition of chlorine dioxide.

Hoather<sup>16</sup> describes some determinations of the solubility of ozone in water. He showed that with some waters reductions in colour, permanganate demand, and count of coliform bacteria, were directly proportional to the amount of ozone added up to a certain point, beyond which there was no change. An interesting description of the use of ozone for treating sea-water in a swimming bath is given by Chadwick,<sup>17</sup> though the paper does not include any detailed estimate of costs. It appears, that, in Illinois,<sup>18</sup> bromine is used as a disinfectant in no fewer than 52 swimming baths. It was originally adopted because of the difficulty in obtaining liquid chlorine during the war; the average amount added daily appears to be about 2.5 to 3 parts of bromine per million parts of water in circulation. Some interesting figures are given by Mallmann and Kahler<sup>19</sup> for the reduction in numbers of coliform bacteria brought about by addition of coagulants and treatment of the water in a Spaulding precipitator with a sludge blanket; the removal was found to be greater in one hour than in four hours with the same coagulants but with sedimentation in a tank of conventional design.

The American Water Works Association<sup>20</sup> has now recommended a standard procedure for disinfecting water mains. For temporary jointing, moulded or tubular rubber rings are recommended; if hemp is used, it should be treated with an organic mercurial compound ("Klerol") or with a quaternary ammonium compound. After the main is laid, water treated with a high concentration of chlorine is allowed to flow slowly through it for at least 24 hours to destroy bacteria and spores; the pipe is then thoroughly flushed with water before being put into service. Some caution in using "Klerol" is necessary, however, for it has been shown<sup>21</sup> that the first water passed through a pipe in which the inner surface and packing material have been treated with this compound may contain undesirable amounts of mercury; the concentration falls rapidly but it is clear that the first flushings should be discarded.

### Corrosion

An investigation by the British Non-Ferrous Metals Research Association of failures of copper water service pipes in the North of England

is described by Tyrrell.<sup>22</sup> There were three main types of action of the water on the metal, all of which could be explained on the assumption that the initial process was the formation of a non-metallic film on the surface of the copper; this might be completely non-permeable and thus protective, or completely permeable, so giving rise to general corrosion, or it might be permeable at a few points and thus give rise to pitting. A very interesting paper by Pallo<sup>23</sup> describes experiments with laboratory-scale steel tanks, provided with different forms of electrical protection, in which quantitative measurements were made of corrosion by water. A sacrificial aluminium anode with an external impressed potential prevented corrosion almost entirely; a sacrificial magnesium anode with no impressed potential considerably reduced attack and prevented it completely after an initial period; but no protection was given by a so-called "electrodeless" circuit. This is a system in which an external potential is applied to the tank wall itself; at opposite ends of one diameter there are two anodic areas, and at opposite ends of another diameter, at right angles to the first, there are two cathodic areas.

### *Softening*

A Committee of the American Water Works Association has reviewed the methods of disposing of lime sludge and gives some particulars of two new types of stationary vertical calcining furnaces which have been introduced recently. It is expected that three full-scale calcining plants will be operating in U.S.A. by 1949.<sup>24</sup> Streicher and others,<sup>25</sup> in a detailed paper, give the results of research during a long period, in the metropolitan water district of Southern California, on the factors affecting the softening of water in beds of synthetic siliceous zeolites. Walker<sup>26</sup> describes the re-introduction of a process, first put forward in 1908, in which water is softened by the lime process and is then passed through an exhausted bed of zeolitic material to remove calcium carbonate from solution and fine suspension. This scheme was impracticable when it was first suggested since in order to remove the calcium carbonate from the exhausted zeolite it is necessary to use acid, which was impracticable with the alumino-silicates which were then used as zeolites. The process can now be worked, however, by using a carbonaceous zeolite, which can be regenerated with acid.

The most important methods now used to obtain substantial removal of both cations and anions from water are treatment with base-exchange and acid-absorbing substances, distillation in multiple-effect evaporators, and distillation in a compression still. The cost of treatment by exchange methods rises rapidly with increasing concentration of salts in the raw water and little information has so far been published on the relative costs of treatment, by the three methods, of water of different composition. A useful though not very detailed paper on this subject has recently been published by Kominek,<sup>27</sup> who states that the cost of treatment in a compression still is less than that of treatment by exchange methods if the raw water contains more than 700 to 900 p.p.m. total solids.

In using molecularly dehydrated phosphates to prevent deposition of calcium carbonate an important factor is the possible precipitation of

calcium orthophosphate. Green and Holmes<sup>28</sup> have discussed quantitatively the factors affecting deposition and give tables, constructed from data published by other authors, from which, for a water of given composition the  $p_H$  value at which tricalcium phosphate will precipitate can be calculated. The basic data are so far rather meagre and there is still considerable uncertainty on the values of the various constants involved.

#### *Silica and dissolved oxygen*

It is frequently necessary to remove silica from water which is to be used in high-pressure boilers; the permissible concentration in the feed water is often about 5 to 10 p.p.m. Three methods of removing silica by chemical means have recently been described. In one,<sup>29</sup> the water is passed through a base-exchange material previously regenerated with acid; a fluoride is then added to the water to react with silica, forming  $H_2SiF_6$  which is removed by a bed of acid-absorbing artificial resin. Fluoride may be added in the form of hydrofluoric acid, sodium fluoride, or calcium fluoride. Calcium fluoride has the advantage of being relatively low in cost but its solubility is low and if it is used it is circulated as a slurry in the water and is passed through the base-exchange filter with some risk of blocking the bed of exchange material. An excess of hydrofluoric acid of about 20 to 40% above the theoretical amount is required. By this method the concentration of  $SiO_2$  in water can be reduced from about 10 p.p.m. to 0.3–0.5 p.p.m., the concentration of fluoride in the treated water being from 0.2 to 0.4 p.p.m. F. A second method described in the same paper, involves the use of a strongly basic anion-exchange material which will remove both  $H_2SiO_3$  and low concentrations of  $CO_2$  from water. Results are given which show that the concentration of silica in water was reduced from 10 p.p.m. to 0.1–0.2 p.p.m. by this means. Another interesting method, described by Leaf<sup>30</sup> depends on the reaction of silica with freshly formed ferric oxide. After small-scale and pilot-scale work a full-scale treatment plant was built, consisting of a cylindrical rotatable drum on a horizontal axis. The water is passed through the drum, which contains cast-iron chips, and the silica reacts with the ferric hydroxide formed by rusting. It is necessary to rotate the drum at intervals of 15 minutes in order to remove the rust from the surface of the iron. No attempt is made to remove the colloidal ferric hydroxide from the treated water since it has been found that its effect is to soften the scale formed in the boiler.

A full-scale plant for removing dissolved oxygen from boiler feed water by addition of sodium sulphite has been described by Pye.<sup>31</sup> It has been found that the reaction is efficiently catalysed by cobalt, which is much more effective than copper for this purpose. In the presence of 0.01 p.p.m. Co the water can be completely de-oxygenated during a period of contact of 15 to 20 seconds.

#### *Lead, manganese, fluorides, etc.*

Evidence has been presented by Miles<sup>32</sup> to show that the plumbosolvency of natural waters increases with increasing concentration of organic matter as determined by permanganate demand. It is clear,

however, that the position has not yet been reached when the plumbosolvency of a water can be predicted with certainty from its composition.

Methods of treating water to remove manganese include precipitation at  $p_H$  values above 9, passage through beds of manganese zeolites, and oxidation followed by filtration. Rawson and Fuller<sup>33</sup> have reported that ozonisation was unsatisfactory in the treatment of water from the Aldenham reservoir of the Colne Valley Water Company, but excellent results were obtained with super-chlorination; this method has now been adopted on a large scale. On the other hand, Whitson<sup>34</sup> found ozonisation to be successful; by treating the water with ozone, filtering through sand, and again treating with ozone, the concentration of manganese was reduced from 0.35 to 0.08 p.p.m.

A detailed review, with a full bibliography, of methods of removing fluorides from water has been given by Maier.<sup>35</sup> For large treatment plants he recommends reduction of fluoride content by lime softening; addition of magnesium compounds may be necessary. For some waters, however, the most satisfactory method may be removal by aluminium hydroxide floc in the presence of a flocculating clay. A detailed dental survey of two areas in New Jersey is described by Klein<sup>36</sup>; in one area, the public water supplies contain from 1.2 to 2.2 p.p.m. F and in the other area fluorides are absent. The effect of fluoride on dental caries is evidently complicated and differs considerably in the different types of teeth; Klein found that the attack in the lower molar teeth is reduced only by about one-third with waters containing fluoride. A Committee of the American Public Health Association<sup>37</sup> has considered the possible effects of other dissolved constituents of water on health and has published a review of the data at present available. There appears to be some evidence that certain American waters may contain sodium, nitrate, and toxins derived from blue-green algae, in concentrations sufficiently high to be harmful.

## Sewage

### Analysis

Several excellent papers have appeared during the year on the evaluation of sewage, particularly by oxidation methods. The whole trend of this work has been to show that the estimation of oxidisable matter in sewage by the test for biochemical oxygen demand, in which oxidation is brought about in part at least by the activity of bacteria, requires complete overhaul. For example, it has usually been assumed that the relation between the rate of oxidation ( $k$ ) and temperature, within the range  $2^\circ$  to  $40^\circ$ , can be expressed by the equation,  $k_T = k_{20} \times \theta^{(T-20)}$  where  $\theta$  is a constant. Gotaas,<sup>38</sup> as a result of some thorough work, has now found that there is a marked fall in the value of  $k$  between  $30$  and  $40^\circ$  and that different values for  $\theta$  are obtained within the temperature ranges  $5^\circ$ – $15^\circ$ ,  $15^\circ$ – $30^\circ$ , and  $30^\circ$ – $40^\circ$ . Moreover, he found (as have several other workers recently) that the value of  $k$  usually taken for sewage ( $0.1$  at  $20^\circ$ ) is often much too low; for the first stage of oxidation before nitrification begins, he obtained an average value of  $0.19$ . It is, indeed, now clear that considerable variations in the course of oxidation may be caused by nitrification during a period of incubation of five days.

When nitrification occurs the relation between up-take of oxygen and period of incubation is by no means expressed by the equation for a unimolecular reaction as it is when only carbonaceous matter is oxidised. Ruchhoft and others<sup>39</sup> have found, as might be expected from previous work, that nitrite is formed at an earlier stage during incubation the lower the concentration of sewage in mixture incubated.

It cannot be said that any agreement has yet been reached on the significance of nitrification in the B.O.D. test. One of the purposes for which results of the test are used is to predict the up-take of oxygen when polluting substances are discharged to a stream. The oxygen absorbed will include any used in the oxidation of ammonia to nitrite or nitrate. It is argued, however, that the nitrite or nitrate will itself constitute a reserve of oxygen, which will be available later for the oxidation of reducing substances, though there is in fact no sound evidence to show what finally happens to nitrate in a stream. Several attempts have been made to suppress nitrification in the test for B.O.D. and thus to determine the oxygen absorbed by carbonaceous matter only. One method proposed is to pasteurise the sewage or effluent before dilution and incubation<sup>40</sup>; another recent suggestion is that the liquid should be acidified before incubation.<sup>41</sup> Abbott<sup>42,43</sup> has found that addition of methylene blue suppresses nitrification, at least in part, but this method is not of universal application since methylene blue also affects oxidation of carbonaceous matter.<sup>44</sup> Ruchhoft and others<sup>45</sup> determine nitrite after incubation and make an allowance for the oxygen involved; they show that when this is done the rate of oxidation during incubation is pseudo-unimolecular but that the value of the constant  $k$  varies over a wide range (0.07 to 0.25 at 20°) for different samples of sewage. It is certainly clear that the assumption which is often made that the value of  $k$  for different sewages is always approximately 0.1 at 20° is incorrect.

There has been some renewed interest in determination of absorption of oxygen by manometric methods. Falk and Rudolfs<sup>46</sup> describe a modification of Sierp's respirometer and discuss the precautions necessary in using it. Caldwell and Langelier<sup>47</sup> have discussed the relative advantages of different types of instruments and have investigated many of the factors involved in determining absorption of oxygen, including frequency of shaking, absorption of carbon dioxide, and dilution of sample. In general, the greater the dilution the lower is the weight of oxygen absorbed in a given time. Respirometer methods have been used in the examination of sewage for many years and it has usually been found that with careful manipulation the results obtained are at least as reproducible as in the dilution method of determination of B.O.D., but it seems unlikely that the method will ever have the precision of a purely chemical determination.

A variation of the method of determination of oxidisable material by digestion with potassium dichromate has been proposed by Ingols and Murray.<sup>48</sup> This consists in distilling under a reflux condenser for 60 minutes a mixture of the sample and a solution containing sulphuric acid, phosphoric acid, potassium dichromate, and selenium as a catalyst, excess dichromate being determined iodometrically. In previous methods of this kind, chlorides have usually been removed before making the

determination. In the present method the concentration of chloride in the sample is determined separately and a correction is applied.

### *Septicity*

Heukelekian,<sup>49,50,51</sup> who has studied reduction of sulphate to sulphide in sewage, confirms that sulphate-reducing bacteria are not normally found in large numbers in sewage itself but are often concentrated in deposits and growths in sewers. When *Sporovibrio desulfuricans* was added to sewage or to sewage containing added sodium lactate, no sulphide was produced. He concludes that sulphate is not reduced until a sufficiently low oxidation-reduction potential is reached, normally as a result of decomposition of organic matter by bacteria other than sulphate-reducing bacteria. He shows that when chlorine is added to septic sewages total oxidation of sulphide does not occur until the whole of the chlorine demand has been satisfied; for fresh sewage, addition of chlorine equivalent to about one-quarter of the demand will normally prevent septicity. Difficulties from septicity appear to be particularly serious in California, where the temperature is high and some of the sewers are very long. Excellent results in preventing septicity in long pressure mains are reported from injection of compressed air; this removes growths of bacteria from the inside of the main, after which formation of sulphide can easily be inhibited.<sup>52</sup> At one works in California,<sup>53</sup> where concrete and brick manholes have been extensively damaged by septic sewage, the brickwork has been covered with thermoplastic synthetic vinyl resins of which three types have been tried. A pump chamber treated with one of these substances has not undergone any deterioration during four years though uncoated concrete was penetrated at a rate of 1-2 in. per year.

### *Sedimentation*

Although the efficiency of sedimentation tanks is of great importance in the treatment of sewage, comparatively little work has yet been done to determine the factors on which efficiency depends. One such investigation, however, has recently been made by George and Manyam,<sup>54</sup> who worked with model tanks and compared hydraulic efficiency for different Froude numbers. Their paper gives only a comparatively brief summary of the results obtained; the full results are presented in two theses deposited in the library of the University of Manchester. Some detailed work with full-scale sedimentation tanks treating sewage has been carried out by Jenkins and others.<sup>55</sup> The most striking result of this investigation was that satisfactory sedimentation was obtained at rates of flow considerably greater than those for which the tanks were designed. No evidence was found that the high velocities caused disturbance of settled sludge under the conditions of these experiments. Sedimentation tanks used in Great Britain are often very much bigger than those in U.S.A. for the same rate of flow of sewage and it is clear that the whole question of design requires examination. A new type of tank built in America has recently been described.<sup>56</sup> In this the incoming liquid enters the tank tangentially in an annulus formed between the circular wall of the tank and a vertical baffle concentric with it; the effluent leaves over a circular notched weir at the centre. Figures for performance have not yet been given.

*Activated-sludge process*

Some years ago the theory that purification of sewage by the activated-sludge process depends to some extent on the ion-exchange properties of the sludge floc was widely discussed. Keefer<sup>57</sup> has now determined the exchange capacity of raw, digested, and activated sludges, in each of which volatile matter was reduced in several stages by heating. He found that the sludges had exchange properties, that activated sludge had a smaller capacity than the other two types, and that the exchange capacity decreased with decreasing content of volatile matter. Further evidence<sup>58</sup> has been presented to show that protozoa may play an important part in the activated-sludge process.

Some interesting work on the efficiency of the paddles used in the "Sheffield" process of treatment by activated sludge has been described by Edmondson and Goodrich.<sup>59</sup> Among the factors investigated were speed of rotation, shape, and length of blades, and depth of immersion of the paddles. By modifying the shape of the blades and depth of immersion the authors were able to improve the efficiency (defined as proportional to weight of oxygen introduced into water for a given input of mechanical energy) by 50%. The "Kessener" type of aeration plant which came into service at Rochdale in 1944 has been described in detail.<sup>60</sup> A little further information is now available on the contact aerators which were built at some army camps in U.S.A. during the war<sup>61</sup>; the first detailed account of these plants was given by the American National Research Council.<sup>62</sup>

*Biological filtration*

For some time the need has been felt for a standard specification for the medium used in percolating filters. This has now been met by the publication of a British Standards Specification.<sup>63</sup> The properties for which tests are provided include size, shape, cleanness, and durability.

The National Research Council of U.S.A. has published a comprehensive report on the performance of 399 sewage-disposal works at camps in America during the war.<sup>62</sup> From a consideration of the performance of percolating filters, some of them operated with very high loadings, the important conclusion is drawn that over a wide range the efficiency of a filter (defined as the proportion of the total weight of applied oxidisable matter removed) is substantially constant, irrespective of the filter loading. This generalisation is discussed and extended by Velz.<sup>64</sup> He compares the performance of filters of different types as determined by experiment with the performance computed from basic data; some of these data (as, for example, the change in rate of oxidation with temperature) are clearly not very reliable but there is a striking concordance between the predicted and ascertained results of operation.

An interesting attempt has been made by Goldthorpe and Nixon<sup>65</sup> to improve the efficiency of a filter by using, as filtering medium, tiles designed to give maximum aeration of the liquid flowing over them. The concentration of dissolved oxygen in water increased from 2.2 p.p.m. to the saturation value in passing through a filter 7 ft. deep containing the tiles, the rate of application being 13,000 g.y.d. The tiles, however, were not as efficient as coke for the treatment of sewage at Huddersfield.

Lumb and Barnes<sup>66</sup> have drawn attention to the effect of periodicity of application of settled sewage to a percolating filter on the growth of biological film. In full-scale circular filters ponding was much greater with an interval of 11 seconds between periodic applications of settled sewage (on any radius) than with intervals of 64 seconds. Some further results of treatment of sewage by filtration with re-circulation of effluent and by alternating double filtration have been given by the Water Pollution Research Laboratory<sup>67</sup>; it has been announced that, in view of the success of alternating double filtration on an experimental scale at Minworth, it is now proposed to operate the whole of the plant by this process.<sup>68</sup>

Rates of growth at different temperatures of a few species of fungi normally found in the biological film of filters have been determined.<sup>69</sup> Reynoldson<sup>70,71,72</sup> studied the distribution of two Enchytraeid worms, *Lumbricillus lineatus* and *Enchytraeus albidus*, in the filters at Huddersfield where the sewage contains acidic chemical wastes. The dominant worm is *E. albidus*, *L. lineatus* being comparatively rare, and he has shown that this is due to the greater susceptibility of *L. lineatus* to the chemical wastes. He found no evidence that there had been any physiological adaptation in the worms in the Huddersfield filters.

### Sludge

Heukelekian and Kaplovsky<sup>73</sup> have studied the digestion of sewage sludge at temperatures of 20, 40, and 50°. They did not isolate the bacteria responsible for digestion but from measurements of gas yield from sludges digested first at one temperature and then at another they concluded that the organisms responsible for digestion at 40 and 50° are similar to but are different from the organisms responsible for digestion at 20°. They suggest that the organisms responsible for digestion at the higher temperatures are facultative thermophilic bacteria with an optimum temperature in a range of about 50° to about 55°. It has been reported during the past few years that sludge for digestion can be heated satisfactorily with live steam. A plant is now described in which it is proposed to heat the sludge by submerged combustion of sludge gas.<sup>74</sup> Experience at Detroit with vacuum filtration of sludge after conditioning with ferric chloride is described by Burley.<sup>75</sup>

The American Federation of Sewage Works Associations has published a very informative and useful summary of American practice in utilisation of sewage sludge as fertiliser<sup>76</sup>; there are about 250 references to literature. It appears that in America there is little sale for digested sludge, most of it being given away and in some cases loaded free of charge, but there is a ready market for heat-dried activated sludge.

A few papers have appeared during the year on pathogenic organisms in sludge. Newton and others<sup>77</sup> worked with the miracidia of *Schistosoma japonicum* at low temperatures (7 to 18°). Digestion of sludge for two to three months is required to render the eggs non-viable; the period decreases with rising temperature. There are two interesting papers<sup>78,79</sup> on a widespread infection of the population of Darmstadt with the round worm *Ascaris lumbricoides*, resulting from the growing of vegetables in fields treated with raw sewage and sewage sludge. Jensen<sup>80</sup> gives a detailed account of the occurrence of tubercle bacilli in sewage from

institutions for patients with pulmonary tuberculosis, and discusses disinfection of sewage effluents with chlorine, and the effect of digestion and drying on the viability of the bacilli in sludge. So far as the reviewer is aware this is the first detailed investigation of this kind of which the results have been published. Unfortunately, the paper is in Danish, but it has an English summary ; a full translation would be very valuable.

## Trade waste waters

### *Coal mining*

The West Riding of Yorkshire Rivers Board have published a detailed report giving particulars of the waste waters (excluding water pumped from mines) discharged from 105 collieries, of which 79 have coal washeries.<sup>81</sup> Although there are many differences in the methods of operation of washeries there are two chief ways of dealing with the washing water : (1) by sedimentation of suspended solids without addition of chemicals, and (2) by sedimentation after addition of flocculating agents, of which mixtures of starch and alkali are most commonly used. Where flocculants are not added, impurities normally accumulate in the liquid which therefore has to be discharged periodically. When flocculants are used, however, the treated waste water contains very little suspended matter and can usually be re-used without any discharge of waste liquid. The importance of dry methods of preliminary de-dusting of coal is again stressed. There does not seem to be any very satisfactory method of treatment of waste waters from coke-oven plants at these collieries ; methods of disposal include use in quenching coke, irrigation on burning spoil banks, and discharge to old pit workings.

Some interesting data on the flow and composition of water pumped from mines is given by Saul<sup>82</sup> ; some of these waters contain ferrous salts and sulphuric acid in solution, and when discharged to a stream ferric hydroxide is often precipitated. It has usually been supposed that oxidation of the ferrous salts was due to purely chemical processes, but work in America now suggests that at least under some conditions bacteria may be concerned in the oxidation. Colmer and Hinkle<sup>83</sup> found that when acidic mine water was sterilised by addition of bactericidal substances oxidation did not occur. They isolated a bacterium (a Gram-negative non-sporing rod) which when inoculated into sterile mine water brought about oxidation.

There is also some evidence that bacterial action plays some part in oxidation of pyrites to ferrous sulphate and sulphuric acid ; Hinkle and Koehler<sup>84</sup> have isolated a bacterium believed to be *Thiobacillus thiooxidans* which may play some part in this reaction.

### *Food industries*

A useful collection of information on the character of waste waters from dehydration of various foods, including milk, whey, and vegetables, is given by DeMartini and others.<sup>85</sup> A noticeable feature, not always sufficiently recognised in designing treatment plant, is the large amount of polluting matter in the condensate from the vacuum concentration of

milk products, particularly of fermented whey. Of the various types of cannery waste, that from the treatment of tomatoes is known to be particularly difficult to deal with. Le Vine<sup>86</sup> had little success in treating these wastes with coagulants; lime used alone was the most satisfactory but the sludge contained less than 0.2% solids and could not be de-watered satisfactorily on a vacuum filter. A full-scale plant in Wisconsin for treating a sewage containing a very large proportion of waste waters from the processing of peas and milk, is described<sup>87</sup>; it includes coarse and fine screens and a percolating filter of unusual type, with specially designed tiles as filtering medium, to be operated with re-circulation of effluent. It is still thought in many parts of America, that the most satisfactory way of disposing of cannery wastes is by lagooning with addition of sodium nitrate to prevent septicity, followed by irrigation on farm land<sup>88</sup>; this process appears to be quite satisfactory where sufficient land is available but would not normally be applicable in Great Britain.

Of the various methods of disposing of distillery wastes, particular attention is being given in America to concentration in multiple-effect evaporators, the concentrate being used for feeding farm animals. A recent paper by Klassen and Troember<sup>89</sup> gives the latest information about the plant of the American Distilling Company at Pekin, Illinois, where this method has been under development for several years. The chief raw materials used are maize, rye, wheat, and malt.

Further data on the volume and character of waste waters from abattoirs in Great Britain<sup>90</sup> and U.S.A.<sup>91</sup> have been published during the year. Various methods have been tried—as a rule with no great success—for recovery of valuable material from these liquors. In a new method described by Sanders<sup>92</sup> the waste waters are treated with sulphuric acid and ferric sulphate at  $p_H$  4.8 and are then passed through a flocculator and sedimentation tank, the sludge from which is heated to about 80 to 90° and is then de-watered on a vacuum filter; it is stated that the material can be fed successfully to pigs when it does not exceed 3% of the total food.

In Great Britain waste waters from dairies and milk products factories are now often treated by alternating double filtration. There are some plants, however, in which the waste waters are treated by addition of coagulant (usually alumino-ferric), the liquid, after separation of sludge by sedimentation, then being further treated in a single-stage percolating filter. Under properly controlled conditions this process, like the process of alternating double filtration, will yield an effluent of good quality.<sup>67</sup> No information has yet been published from which the relative costs of treatment by the two methods can be compared.

Very little information has hitherto been available on the treatment of waste waters from the manufacture of cider. It had been suggested that these liquors were difficult to treat either alone or in admixture with sewage, because they so rapidly become acidic on storage. Experiments in pilot-scale plant at the Water Pollution Research Laboratory,<sup>67</sup> however, do not confirm this; when diluted cider was mixed with sewage the mixture could be treated in percolating filters as readily as sewage, containing the same amount of organic matter, alone. The outstanding characteristic of cider wastes is their very high C : N ratio; if they are to be treated alone by a biological process it is necessary to add nitrogen,

for example, in the form of an ammonium salt; effluents of good quality can then be obtained.

During recent years the growth of industry in East Africa has given rise to some problems of pollution, particularly since, in the dry season, the water supply is very limited. One of the biggest problems arises in the processing of coffee. The coffee cherries (each of which contains two coffee beans) are split and the greater part of the soft tissues is removed mechanically. A certain amount of pulp, however, still adheres to the beans and this is removed by allowing it to ferment and then washing it away with water. Finally, the beans are classified hydraulically into heavy and light fractions. These operations give rise to a strongly polluting liquor, most of which has hitherto been discharged to a stream. It has now been shown<sup>67</sup> that the waste waters, after treatment in a percolating filter, can be re-used in the process without significantly affecting the quality of the coffee. If such a method were adopted on a large scale it would at once avoid the discharge of polluting matter and would reduce very considerably the volume of water used in the process.

#### *Pulp and paper*

In spite of the great amount of research which has been carried out on the economic disposal of sulphite liquors no effective process has yet come into general use. Lewis<sup>93</sup> has reviewed the present position. Among the more important methods of treatment which are being considered are concentration (to allow of subsequent incineration) by the Ramón and Rosenblad processes, which are designed to avoid the formation of scale during evaporation, use of ammonia-base liquors which can be concentrated and burned without scaling, use of calcium-base waste liquors in the manufacture of cement and ceramics, and preparation of tanning materials. Lewis estimates that the potential market in America for tanning materials is equivalent to about 10% of the waste liquor available there. Recovery of alcohol after fermentation is now a well-established process, particularly in Scandinavia, though it does not greatly ease the problem of ultimate disposal of the waste. Lewis considers that production of alcohol from sulphite liquors in U.S.A. would probably not have been economic under pre-war conditions. There are many references to fermentation of sulphite liquors to yield products other than alcohol. Methods for recovery of lactic acid<sup>94</sup> and butyric acid,<sup>95</sup> at present in the development stage, have been described.

A very interesting method of treatment, not involving recovery of valuable materials, has been described by Logar and Heukelekian.<sup>96</sup> They found that when sulphite liquor, inoculated with bacteria, was aerated with diffused air or with oxygen, little oxidation of organic matter occurred. When ammonium salts and phosphates were added, however, and the rate of aeration was greatly increased so that the liquid, contained in a tall tower, foamed copiously, there was rapid oxidation, the biochemical oxygen demand being reduced during 24 hours by over 80%. A mat-like tough growth containing fungi, bacteria, and yeasts, developed on the inner surface of the tower. It appears that this method has not yet been tried on a large scale.

A large amount of work has been reported from America during the year on waste waters from paper mills and board mills; this has been concerned mainly with removal of suspended matter by addition of coagulants and sedimentation or by filtration.<sup>97,98,99</sup> It has been shown<sup>100</sup> that, in determining the biochemical oxygen demand of these liquors, it is necessary to add nutrient substances, including a source of nitrogen. There are two important papers on biological methods of treatment. Gehm<sup>101</sup> has confirmed the conclusion drawn from some British work carried out a few years ago that paper mill wastes can be treated satisfactorily in percolating filters; he found that oxidation was much more rapid at 28° than at 19°. Buswell and Sollo<sup>102</sup> have shown that a waste liquor from a fibre-board factory can be treated satisfactorily by anaerobic fermentation; the nutrient substances added included magnesium, potassium, phosphate, and ammonia. In laboratory experiments a reduction in B.O.D. of 94% was obtained by digestion in two-stage digestors with a total period of retention of five days. The authors estimate that the cost of treatment by this means would be less than 8% of the cost of treatment in percolating filters. A full-scale plant is being designed. The waste waters examined were from a mill at which pulp is prepared from wood by the action of steam only; there was no difficulty, therefore, from excessive alkalinity in the wastes.

### *Textiles*

A detailed account of the work which led to the development of the aerated process of flax retting has now been published.<sup>103</sup> This report reviews previous work on the composition and treatment of waste waters from retting, describes trials of anaerobic retting and treatment of the waste waters by different methods, and describes experiments with pilot-scale and large-scale plant on the retting of flax by anaerobic and semi-aerobic methods. With the method of retting finally adopted, employing aeration of the liquor in the retting tank, there is normally no discharge of waste waters. The report includes the results of a considerable amount of microbiological work on the retting process. Although retting with aeration was suitable for the flax fibre required during the war, it was uncertain whether it would be used on a large scale in peace time. A recent paper by Gibson,<sup>104</sup> however, indicates that the fibre obtained by this method is not inferior to that obtained by the anaerobic methods previously used. If the growing of flax becomes established in Great Britain it will be a great advantage if retting with aeration can be adopted, since there would be considerable difficulty in disposing of the polluting liquors from anaerobic retting. On the Continent much pollution has been caused by these liquors, the disposal of which is one of the major problems confronting the industry.

A problem which has recently become of importance in the textile industry is the treatment and disposal of waste waters containing synthetic detergents which are now being used on a large scale in place of soap, particularly for the washing of wool. In Yorkshire (as in Germany<sup>105</sup>) reasonably effective methods of dealing with waste washing waters containing soap have been developed; many of the liquors are treated with acid at the mill to recover grease, which is also recovered at some

sewage-disposal works (particularly at Bradford) where the sewage contains particularly large proportions of waste liquors. It appears, however, that the methods at present in use may not be satisfactory for waste waters from mills where synthetic detergents are used. This question was discussed by various authors in a symposium organised by the Institute of Sewage Purification.<sup>106</sup> It seems to be now established that when sewage contains synthetic detergents rather than soap, the proportion of the oxidisable matter which can be removed in primary sedimentation tanks is much reduced; the effect of the new detergents on biological processes of treatment has not yet been determined. The problem may become of more general importance if the present trend of replacing soap by synthetic detergents for household purposes continues.

A process similar to that already described for the treatment of waste waters from the processing of coffee has been developed for the waste liquor discharged in East Africa from the extraction of fibre from sisal.<sup>67</sup> This process has been operated without difficulty in pilot-scale plant.

#### *Other industries*

Treatment of cutting oils by addition of salts of multivalent metals (as, for example, aluminium sulphate) is now being increasingly used in Great Britain. Eldridge and Purdy<sup>107</sup> in America have confirmed that sodium chloride is not very satisfactory for this purpose; they obtained good results with a particular type of cutting oil by adding calcium chloride and then, in a second stage, lime and ferric sulphate. Kalinske<sup>108</sup> has developed an interesting method for treating oil refinery wastes; he adds waste sludge from a water-softening plant and treats the mixture in a plant of the "Accelerator" type. The oil content of the waste was reduced from an average of 300 p.p.m. to less than 30 p.p.m.; the sludge is easily de-watered and can be burnt without additional fuel. A very useful collection of papers on treatment of waste waters from petroleum refineries has been published during the year<sup>109</sup>; it includes a bibliography of 174 references.

Waste waters containing cyanides are being treated in full-scale plants in America by addition of chlorine<sup>110</sup>; so far, however, the descriptions published have been of a very general kind and there is no information on the precautions which would be necessary to ensure that the treated wastes contained neither an excess of cyanide nor chlorine. This problem is being attacked also in this country and is believed to be nearing solution. Some further information on the treatment of cyanides with ferrous sulphate, by which the cyanide can be greatly reduced in amount, though not entirely removed, has been given by the Water Pollution Research Laboratory.<sup>67</sup>

There is an interesting paper by Landau and Rosen<sup>111</sup> on a process for removing fluorine and hydrofluoric acid from gases. The gases are passed upwards through a tower at a temperature of 38 to 66° against a downward flow of a 2% solution of sodium hydroxide. The liquid is passed through a reaction tank to which lime slurry is added continuously to regenerate sodium hydroxide and to precipitate calcium fluoride.

### Effects of pollution

Some much-needed work has been done by Jones<sup>112</sup> on the reactions of fish in water containing toxic substances; these include acids and alkalis, sulphides, lead, and ammonia. The results confirm those of Shelford and others, obtained more than 30 years ago, that although fish will swim from toxic concentrations of some substances, they swim into toxic concentrations of others; this is often of great importance in a fishery where a particular stretch of a river, or sometimes water near one bank in the neighbourhood of an outfall, contains poisonous substances. Ellis<sup>113</sup> has determined the toxicity to fish of phenyl-mercuric lactate (used in the pulp industry as a bactericide) and Prescott<sup>114</sup> has shown that decomposition products of some species of blue-green algae are toxic; his preliminary results indicate that the products include hydroxylamine and hydrogen sulphide. There is a useful paper by Hasler,<sup>115</sup> with a good bibliography, on the changes brought about in lakes by discharge of organic matter to them. Kittrell and Kochitzky<sup>116</sup> have studied the oxidation of organic matter in a heavily polluted stream. One of the most important findings from this investigation is that the rate of oxidation, as determined in the test for biochemical oxygen demand, varies considerably for water taken at different distances below an outfall. The authors suggest that some part of the polluting material may have been decomposed anaerobically or may have escaped oxidation in some other way. It seems clear, however, that the rate of oxidation of different constituents of a polluting liquid varies over a considerable range.

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# NAME INDEX

## A

- Aagaard, L., 193  
 Abbot, 317, 321  
 Abbott, W. E., 658, 668  
 Abeele, F. R. van, 599  
 Abernethy, R. F., 212, 215  
 Abramson, I. D., 293  
 Acree, 451  
 Adam, W. B., 534, 543  
 Adams, C. H., 24  
 Adams, M. E., 253, 262  
 Adams, S. L., 566, 571  
 Addoms, J. N., 10  
 Adelsohn, 649  
 Adkins, H., 574, 599  
 Adler, M., 617  
 Adolph, W. H., 466, 469  
 Aelion, R., 366  
 Afanasen, N. M., 631  
 Agarwal, R. N., 504, 516  
 Agey, W. W., 145  
 Aggarwal, J. S., 254  
 Agnew, (Sir) A., 228, 234  
 Agronin, T., 329  
 Ahmad, 321  
 Aichholzer, W., 115, 125  
 Aiken, 319, 321  
 Aiken, W., 372  
 Ainsworth, G. C., 566, 571, 600  
 Ainsworth, M., 440, 478  
 Air Reduction Co., 70, 192  
 Airan, J. W., 254  
 Aitchinson, A. G., 167, 190  
 Akel, R. R., 13  
 Akker, J. A. van den, 335  
 Alba, R. T., 568  
 Albert, A., 555, 568  
 Albert, H. E., 418  
 Albertson, N. F., 586  
 Alden, R. C., 231  
 Alexander, A. L., 393, 417  
 Alexander, C. H., 342  
 Alexander, H. L., 162  
 Alexander, O. R., 543  
 Alexander, P. P., 193  
 Alexander, W. A., 83, 94  
 Alfrey, T., 372  
 Alibert, J., 29  
 Alink, 648, 651  
 Allan, J., 364  
 Alleane, 518  
 Allen, 441, 451  
 Allen, A. G., 260, 272  
 Allen, C., 396, 397  
 Allen, E. E., 565, 571  
 Allen, F. M., 178, 192  
 Allen, F. E., 491  
 Allen, F. W., 530, 542  
 Allen, G. L., 182, 193  
 Allen, J. F., 110, 124  
 Allen, J. S., 631, 632  
 Allen, L. A., 513, 518  
 Allen, R. J. L., 543  
 Allen, W. S., 172, 191  
 Allenby, W. E., 233  
 Allied Chemical & Dye Corp., 72  
 Allison, C., 669  
 Allison, F. E., 463, 464  
 Allmanna Svenska Elektr. Aktieb., 193  
 Alm, R. M., 77  
 Alquist, F. N., 73  
 Altman, R. F. A., 415, 416  
 Altsheler, W. B., 565, 571  
 Aluminium Co. of America, 193  
 Aluminium Development Assoc., 160  
 Alway, F. J., 466, 469  
 Ambler, J., 519  
 Ambrose, E. R., 214  
 Amer. Ceramic Society, 271, 273  
 Amer. Cyanamid Co., 75, 76, 84, 85, 86, 89, 98, 99, 100, 192, 193, 365, 384, 386, 433  
 Amer. Electro-Platers Society, 153  
 Amer. Oil Assoc., 629  
 Amer. Polymer Corp., 416  
 Amer. Public Health Assoc., 657, 668  
 Amer. Viscose Corp., 68, 375  
 Amer. Waterworks Assoc., 654, 667  
 Amer. Zinc, Lead, Smelting Co., 192  
 Amero, H. C., 23  
 Ammon, M. G., 284  
 Amon, S., 13  
 Ananenko, N. H., 600  
 Anastasevich, 634, 649  
 Anderau, 634, 649  
 Anderberg, R. G., 184, 193  
 Anderson, 441, 451  
 Anderson, C. T., 145  
 Anderson, E. A., 162  
 Anderson, G. W., 523, 540  
 Anderson, H. W., 617  
 Anderson, J. B., 331  
 Anderson, J. T., 194  
 Anderson, L. E., 577  
 Anderson, R. C., 601  
 Anderson, W. T., 174, 191  
 Andriesen, N., 557, 569  
 Andrew, J. H., 113, 125  
 Andrews, A. I., 292  
 Andrews, J. S., 469  
 Andrews, K. W., 141, 146

Andrews, S. W., 11  
 Andrews, W. B., 459, 464  
 Andrus, R. J., 30  
 Anellis, A., 571  
 Angell, H. R., 467, 469  
 Angier, R. B., 600, 601  
 Angles, R. M., 162  
 Anglo-Iranian Oil Co., 72  
 Anish, 641, 650  
 Anker, H. S., 618  
 Anner, G., 593, 595  
 Antoniani, A., 172, 191  
 Appling, J. W., 331  
 Arceneaux, G., 512, 518  
 Archer, S., 586  
 Ardenne, M. von, 292  
 Arend, A. G., 222, 233  
 Arend, H., 161  
 Arens, 640, 650  
 Arenz, B., 456  
 Argyle, A., 118  
 Aries, R. S., 219, 233  
 Armour & Co., 253  
 Armstrong, L. N., 506, 516  
 Arnaudi, C., 559, 569  
 Arnold, 646, 651  
 Arnold, M. H. M., 7  
 Arnold, S. M., 146  
 Arnstein, H. R. V., 583, 618  
 Aronovsky, S. I., 322, 323  
 Arroyo, R., 517  
 Arth, G. E., 601  
 Arthur, J. M., 450  
 Artigas, C. M., 571  
 Arup, P. S., 526, 541  
 Asenjo, C. F., 538, 545, 558, 569  
 Asplin, F. D., 491  
 Assoc. of Tar Distillers, 56  
 Astbury, W. T., 295, 308, 421, 433  
 Aston, R. N., 667  
 Astrup, T., 561, 570  
 Atkin, L., 556, 558, 564, 569, 571  
 Atsuki, K., 369  
 Attenburrow, J., 586  
 Audibert, A., 213  
 Audibert, R., 202, 213  
 Audrieth, L. F., 164, 190  
 Aulabaugh, S. J., 300, 307  
 Ault, W. C., 254  
 Austin, H., 194  
 Austin, J. B., 115, 125  
 Auten, R. W., 365  
 Autoxygen, Inc., 73  
 Auty, C. M., 31  
 Avery, R. C., 618  
 Awapara, J., 544  
 Axelrod, A. E., 568  
 Axon, H. J., 146  
 Ayers, L. R., 334  
 Ayres, F. D., 176, 191  
 Aysel, T. E., 571  
 Azbe, V. J., 176, 192  
 Azim, M. A., 598

## B

Baars, G., 56  
 Bachman, G. B., 340, 348, 350  
 Bachman, G. S., 258, 269, 271, 273  
 Bachmann, W. E., 593, 594  
 Bachner, E. F., 370  
 Bachrach, H. L., 542  
 Back, T. M., 499, 551, 568  
 Bacon, R. C., 393  
 Badenhuizen, N. P., 500  
 Badgley, W. J., 386  
 Bäckström, 636, 649  
 Bai, M. P., 556, 569  
 Bail, J., 545  
 Bailey, A. S., 583  
 Bailey, E. M., 230, 234  
 Bailey, J., 342  
 Bailey, J. C., 232, 529, 542  
 Bailey, K., 422, 433, 552, 568  
 Bailey, L. F., 434  
 Bailey, N. P., 5  
 Bailey, W. A., jun., 193  
 Bainbridge, J. R., 210, 215  
 Baird, E., 193  
 Bakelite Corp., 355, 364  
 Bakelite Ltd., 365, 387  
 Baker, 446, 452  
 Baker, M. D., 26  
 Baker, W. A., 133, 134, 145  
 Baker, W. O., 360, 366  
 Baker & Co., Ind., 190  
 Balandin, A. A., 350  
 Balavoine, P., 539, 545  
 Balch, R. T., 518  
 Balden, A. R., 161  
 Baldock, H., 398  
 Ballard, J. H., 222, 233  
 Baldwin, A. R., 254  
 Baldwin, W. J., 283  
 Balfe, M. P., 423, 433  
 Balfour, B. G., 555, 568  
 Baliga, M. N., 254  
 Ball, 437  
 Ballard, S. A., 364  
 Balls, A. K., 551, 568  
 Bamberger, E., 95  
 Banasik, O., 501  
 Banerjee, S., 545  
 Banfield, T. A., 123, 126, 392, 393  
 Bang, H., 82, 94  
 Bangham, D. H., 23, 212  
 Banier, R., 507, 517  
 Banister, A. W., 669  
 Bank, H., 395  
 Banks, A., 522, 540  
 Banner, 636, 649  
 Baragwanath, G. E., 214  
 Barail, L. C., 430, 434  
 Barbacki, S., 566  
 Barber, G. W., 443  
 Barber, S. A., 464, 466, 469  
 Bard, J. W., 327

- Bardwell, J., 293  
 Barer, R., 421, 433  
 Barham, H. N., 494, 496  
 Barinova, R. A., 470  
 Barker, H. A., 559, 570  
 Barker, J., 530, 542  
 Barker, L., 211  
 Barker, S. A., 498, 567  
 Barlow, F., 438  
 Barlow, R. B., 597  
 Barnebey, H. L., 253  
 Barnes, H., 123, 126, 392, 393  
 Barnes, H. M., 545  
 Barnes, J. B., 661, 668  
 Barnett, G. R., 668  
 Barnett, S. F., 491  
 Barnicoat, C. R., 525, 541  
 Barr, T., 255, 569  
 Barr & Stroud, Ltd., 7  
 Barratt, E. V., 293  
 Barrett, C. S., 135, 146  
 Barrett, J., 308  
 Barrett, J. W., 308  
 Barritt, R. J., 43  
 Barry, G. T., 573, 600, 617, 618  
 Barta, R., 292  
 Bartels, H. A., 626, 632  
 Bartley, W. C., 491  
 Barton, H. M., 417  
 Barton, K., 210, 215  
 Bartz, Q. R., 577, 618  
 Basak, N. G., 233  
 Bashford, T. C., 535, 543  
 Basic Magnesium Inc., 179, 192  
 Basic Refractories Inc., 192  
 Bass, S. L., 366  
 Baston, C. E., 214  
 Basu, A. N., 199, 212  
 Basu, K. L., 516  
 Basu, N. K., 632  
 Batchelor, 482, 483  
 Bateman, E. W., 478, 572  
 Bateman, R. L., 217, 232  
 Bates, 643, 650  
 Bates, R. W., 253  
 Bates, T. F., 259, 272  
 Batisse, M., 136, 146  
 Batjér, L. P., 472  
 Batra, P. C., 324  
 Battecock, W. V., 214  
 Battelle Memorial Institute, 139, 156  
 Battershill, F. J., 232  
 Batty, J. V., 144, 145  
 Bauermeister, G., 193  
 Bauernfeind, J. C., 542  
 Baum, C. E. H., 232  
 Baum, M., 327  
 Bauman, W. C., 25  
 Baume, N., 292  
 Baumgartner, J. C., 533, 543  
 Baumhögger, W., 669  
 Baur, K., 541  
 Baur, P., 330  
 Bavley, 646, 651  
 Bawden, E. F., 567  
 Bawden, R., 547  
 Baxter, G. P., 119, 126  
 Bay Chemicals Co., 191  
 Bayfield, E. G., 528, 542  
 Beadle, B. W., 253  
 Beal, 647, 651  
 Bean, 613, 650  
 Bear, F. E., 469  
 Beard, F. H., 567  
 Beattie, H. G., 532, 543  
 Beaty, A., 528, 542  
 Beaudoin, R. E., 668  
 Beaujard, L., 137, 146  
 Beaven, E. S., 546  
 Beaver, C. E., 326  
 Bechtel, W. G., 500  
 Beck, P. A., 136, 146  
 Beck, Koller & Co. (Eng.), Ltd., 386, 387  
 Beckel, A. C., 253  
 Becker, D. E., 170, 545  
 Becklev, V. A., 566, 572  
 Beckmann, P., 226, 234  
 Beckord, O. C., 501  
 Beckwith, N. P., 395  
 Bedford, C. L., 533, 543  
 Bedoukian, P. Z., 632  
 Boerwald, A., 162  
 Behr, E. A., 335  
 Bohrens, O. K., 599, 610, 617  
 Bejambes, M., 541  
 Bekkedahl, N., 416, 418  
 Belcher, R., 215  
 Belneft, N., 143, 147  
 Belie, H. J., 119, 126  
 Bell, A., 451  
 Bell, A. D., 222, 233  
 Bell, D. J., 508, 517  
 Bell, H. S., 230  
 Bell Telephone Lab. Inc., 141, 146, 376  
 Beloian, E., 272  
 Belter, P. A., 253  
 Belval, H., 518  
 Belyaev, A. I., 160  
 Beman, W. A., 327  
 Bender, C. B., 509, 517  
 Benham, G. H., 570  
 Benjamin, L. P., 161  
 Benk, J. F., 540  
 Benning, A. F., 398  
 Bennitt, J. H., 365  
 Benson, H. K., 327, 328  
 Benthier, K., 133, 145  
 Bentley, H. R., 485, 487  
 Benton, E. D., 215  
 Benz, J., 579  
 Berber, K. C., 474  
 Berchet, 314, 321  
 Berg, 635, 636, 649  
 Berg, C., 15, 222, 233, 398  
 Berg, L., 350

Bergdahl, A. M., 546  
 Berge, S., 294  
 Bergen, H. S., jun., 395  
 Berger, J. H., 169, 191  
 Berglund, V., 563, 571  
 Bergmann, F., 597  
 Bergström, S., 526, 541  
 Berk & Co., F. W., 168, 190  
 Berkowitz, N., 23, 212  
 Berndt, F., 360, 366  
 Bernfeld, P., 497, 501, 550, 567  
 Bernheim, F., 576  
 Berns, M. H., 293  
 Bernstein, I. M., 254, 380, 382  
 Bernstein, J., 109, 124  
 Berriman, 649  
 Berry, C. E., 233  
 Berry, P. A., 630, 631, 632  
 Berthe, 518  
 Bertrand, D., 482, 483  
 Besson, M., 561, 570  
 Bethel, 441, 451  
 Bettelheim, L., 355, 364  
 Betteridge, W., 117, 125  
 Bevan, E. A., 383, 386, 387  
 Bever, M. B., 105, 124, 162  
 Beveridge, C. G., 491  
 Beveridge, J. M. R., 523, 541  
 Beyaeret, M., 567  
 Beyler, R. E., 584  
 Bhagvat, K., 537, 544  
 Bhargava, M. P., 324  
 Bhat, 312, 320  
 Bhatnagar, M. S., 357, 365  
 Bhatnagar, S. S., 598  
 Bhattacharji, S., 632  
 Bhattacharya, G., 545  
 Bhide, B. V., 254  
 Bhushan, B., 632  
 Bianchi, G., 162  
 Bickel, A. F., 587  
 Bickford, W. G., 253, 254, 526, 541  
 Bide, A. E., 604, 616  
 Bie, G. J. van der., 404, 416  
 Bienvenn, R. J., 518  
 Bierce, E. C., 168, 190  
 Biggs, J. D., 166, 190  
 Bikerman, J. J., 267, 272  
 Billen, G. N., 385, 387  
 Billeter, J. R., 595, 602  
 Billman, J. H., 587  
 Biltez, 635, 649  
 Binder, R. C., 5  
 Bingham, J. B., 517  
 Binkley, S. B., 617  
 Binkley, W. W., 508, 517  
 Birch, S. F., 233  
 Birchall, H., 27  
 Birkinshaw, J. H., 619  
 Birks, F. M., 48  
 Birnbaum, L. S., 393  
 Birnthal, W., 343  
 Biserte, G., 422, 433

Bishmann, L. C., 10  
 Bishop, E., 126  
 Bishop, E. L., 451  
 Bishop, L. R., 547, 557, 560, 566, 569, 570  
 Bishop, T., 105, 117, 124  
 Bissell, E. S., 21, 22, 34  
 Biswas, B., 254  
 Bitterfeld, 650  
 Bittner, C. W., 193  
 Black, C. E., 308  
 Black, E., 517  
 Black, G., 162  
 Black, H. C., 254  
 Black, I. A., 483  
 Black, M. V., 259, 272  
 Blackburn, S., 299, 308, 423, 433  
 Blackith, R. E., 450  
 Blackman, C. E., 381, 468, 469, 470  
 Blackman, W., 365  
 Blackwood, A. C., 565, 571  
 Blair, T. S., 162  
 Blake, 649  
 Blake, K. B., 543  
 Blanchard, K. C., 618  
 Blank, O. V., 118, 119  
 Blankmeyer, H. C., 565, 571  
 Blanter, M. E., 117, 125  
 Blaschke, 350  
 Blegen, J. R., 417  
 Blessing, W. H., 326  
 Blickle, R. A., 451  
 Bliss, E. A., 577  
 Bliss, L. A., 417  
 Bloch, R. G., 588  
 Blocher, J. M., jun., 145  
 Block, S. S., 450  
 Blockmann, A. F., 365  
 Blodgett, E. O., 212  
 Blodgett, K. B., 268, 272  
 Blom, J., 550, 561, 567, 570  
 Blom, R. H., 502, 567  
 Blomquist, A. T., 628, 632  
 Bloodgood, D. E., 324, 669  
 Bloom, A., 596  
 Bloom, M. C., 193  
 Bloom, R. C., 333  
 Blount, E. R., 347  
 Blumberger, J. S. P., 81, 93  
 Blumenkranz, N. M. H., 532, 533  
 Blumenthal, L. M., 346  
 Boake Roberts & Co, Ltd., A., 255  
 Boas, W., 135, 146  
 Bobranski, B., 585  
 Böckmann, O., 160  
 Böhme, H., 632  
 Boer, H., 182, 193  
 Bogart, M. J., 13  
 Bogolovski, B. M., 81, 93  
 Bogue, R. H., 291  
 Bohonos, N., 618  
 Bohstedt, 441, 451  
 Bollen, W. B., 457

- Boller, A., 600  
 Bolley, D. S., 381  
 Bolton, H. L., 192  
 Bolton, W., 484, 487  
 Bomshtein, E. I., 181, 192  
 Bonilla, C. F., 7, 8, 10  
 Bonner, J., 416  
 Bonnet, J., 548, 567  
 Boon, W. L., 49  
 Boonstra, B. B. S. T., 418  
 Booth, R. B., 180, 192  
 Booth, S., 371  
 Booth, V. H., 544  
 Boothe, J. H., 600, 601  
 Borasid, L., 542  
 Borasky, R., 421, 433  
 Borchers, O., 540  
 Borchers, R., 537, 545, 568  
 Borden Co., 365  
 Borders, A. M., 416  
 Borg, E. L., 416  
 Borghetty, H. C., 300, 307  
 Boruff, C. S., 565, 571  
 Borum, O. H., 586  
 Borysowski, L., 346  
 Borysowski, Z., 266, 272  
 Bosanquet, N., 517  
 Bosch, 645, 651  
 Bost, R. W., 73, 77  
 Bosworth, R. C. L., 32  
 Bothmann, H., 132, 145  
 Bottger, G. R., 450  
 Boucher, D. F., 6  
 Boulanger, P., 422, 433  
 Bould, C., 462, 463, 464  
 Boulton, 318, 321  
 Bouncy, R. H., 366  
 Bourne, E. J., 498, 499, 503, 567, 570  
 Bousfield, E. G., 559, 570  
 Bowater, E. J. C., 232  
 Bowden, F. P., 227, 234  
 Bowden, J. S., 109, 124  
 Bowden, S. T., 225, 234  
 Bowell, S. T., 418  
 Bowen, K. W. J., 116, 125  
 Bowers, A. E., 668  
 Bowes, J. H., 430, 433, 434  
 Bowes, P. C., 494  
 Bowles, J. S., 135, 146  
 Bowles, O., 176, 192  
 Bowman, R. R., 285  
 Boxer, G. E., 618  
 Boyd, M. L., 364  
 Boyer, H. E., 116, 125  
 Boyer, R. F., 372  
 Boyland, E., 491  
 Boyle, 369  
 Brabender, G. J., 327  
 Bracken, A. F., 466, 469  
 Bracken, W. O., 371  
 Bradford, B., 451  
 Bradish, C. J., 22  
 Bradley, T. F., 380, 382, 398  
 Bradley, W. E., 222, 233  
 Bradley, W. F., 277  
 Bradney, L., 668  
 Braendle, H. A., 417  
 Bragg, (Sir) L., 141, 146  
 Brain, C. M., 22  
 Braley, A. E., 618  
 Brandenburg, E. H., 292  
 Brandt, P. L., 396, 397  
 Brannon, L. W., 450  
 Branton, C., 484, 487  
 Brande, R., 486, 488  
 Braun, H., 538, 545  
 Braun, W. G., 233  
 Brehm, W. J., 583  
 Bremner, J. G. M., 398  
 Bremner, J. M., 455  
 Bremner, T. S., 560, 563, 570, 571  
 Brennan, J., 188, 194  
 Brenner, 310, 320  
 Brenner, A., 161, 162  
 Brenner, P., 146  
 Brenner, S., 545  
 Bressey, R. J., 232  
 Bretagne, R. H. L., 99  
 Bretscher, E., 600  
 Breuniche-Olsen, H., 517  
 Brewer, R. E., 213  
 Brice, N., 483  
 Bridger, G. L., 22, 167, 190  
 Briggs, D. R., 542  
 Briggs, H. M., 488  
 Briggs, L. H., 631, 632  
 Briggs, L. J., 517  
 Briggs, P. S., 427, 434  
 Brightwell, S. T. P., 543  
 Brimm, E. O., 192  
 Brink, N. G., 599, 601  
 Brinkley, S. R., 28  
 Brinn, M. S., 9  
 Brit. Celanese, Ltd., 71, 88, 89, 92, 93,  
 97, 371, 375, 376, 395  
 Brit. Coke Research Assoc., 44, 201  
 Brit. Industrial Solvents, Ltd., 74  
 Brit. Intelligence Objectives Sub-  
 Commee., 162, 163  
 Brit. Non-Ferrous Research Assoc.,  
 140, 143  
 Brit. Rubber Development Board,  
 412, 418  
 Brit. Standards Institute, 359, 365  
 Brit. Thomson-Houston Co., Ltd., 188,  
 194, 365, 366, 386  
 Britton, S. G., 390  
 Broadhurst, J. W., 28  
 Brochard, J., 290, 294  
 Broucker, J. F., 388, 393  
 Brockington, C. F., 207, 214  
 Brode, W. R., 82, 94, 629, 632  
 Broderick, T. C., 28  
 Broeg, C. B., 518  
 Broek, C. J. H. van den, 522, 523, 540  
 Bromberg, 647, 651

- Brøndum-Nielsen, H., 261, 272  
 Broodgraan-en Broodcommissie, 528, 542  
 Brooker, 641, 642, 650  
 Brookes, A., 386  
 Brooks, 441, 451  
 Brooks, L. J., 393  
 Brooner, G. H., 222, 233  
 Broquist, H. P., 568  
 Brown, 313, 320, 447, 452, 649  
 Brown, A. C., 253  
 Brown, A. W. A., 451  
 Brown, A. E., 296, 297, 307, 308  
 Brown, A. M., 571, 600  
 Brown, B. A., 465, 469  
 Brown, B. M., 546, 566, 567  
 Brown, C. A., 518  
 Brown, E., 617  
 Brown, E. H. C., 565, 571  
 Brown, E. V., 599  
 Brown, F., 562, 570  
 Brown, G. B., 533, 543  
 Brown, G. G., 231  
 Brown, H., 557  
 Brown, H. T., 569  
 Brown, J. B., 427, 434  
 Brown, J. P., 619  
 Brown, J. W., 617  
 Brown, L. E., 541  
 Brown, R. A., 184, 193, 224, 233, 545  
 Brown, R. K., 368  
 Brown, R. L., 23, 24  
 Brown, W. E., 565, 571  
 Brown, W. W., 325  
 Brownell, L. E., 6  
 Browning, W. C., 327  
 Brownlee, G., 491, 576, 600, 618  
 Brownlee, H. J., 396, 397  
 Brownlee, K. A., 612, 618  
 Bruce, J., 233  
 Bruckner, H., 27  
 Bruk, A. S., 213  
 Brun, H., 499  
 Brundrit, D., 342  
 Brunjes, A. S., 13  
 Brunner, R., 571  
 Bruno, 649  
 Brusset, 311, 320  
 Brutschy, F. J., 599  
 Bryan, A. M., 212  
 Bryan, J., 462, 464  
 Bryan, J. M., 534  
 Bryan, L. A., 385, 387  
 Bryant, E. E., 284  
 Bryant, L. R., 472  
 Bryce, W. A., 541  
 Bryer, M. S., 577  
 Bryns, C., 193  
 Bubl, J. L., 571  
 Buch, F. E., 145  
 Buchanan, R., 466, 469  
 Buchta, E., 594  
 Buck, F. R., 233  
 Buck, R. E., 531, 543  
 Buck, R. R., 617  
 Buckingham, J., 192  
 Buckley, D. J., 411, 418  
 Buckley, G. D., 398  
 Buckner, A. J., 438  
 Buddin, W., 469  
 Büchi, G., 632  
 Bürki, 643, 650  
 Büttner, G., 540  
 Bugge, P. E., 24  
 Buhle, E. L., 618  
 Buhs, R. P., 574  
 Buist, J. M., 418  
 Bull, J. P., 366, 518  
 Bullock, 636, 649  
 Bulwer, E., 302, 308  
 Bunker, H. J., 512, 518, 559, 569  
 Bunn, C. W., 303, 308  
 Bunting, E. N., 292  
 Burch, C. R., 17  
 Burch, J. E., 491  
 Burckhardt, L. A., 26  
 Burckholder, P. R., 577  
 Burda, E. J., 253  
 Burdick, E. M., 631, 632  
 Burdick, R. B., 285  
 Burgers, 637, 649  
 Burgers, W. G., 135  
 Burgoyne, J. H., 494  
 Burke, J. F., 169, 190  
 Burkhardt, B. A., 564, 567, 571  
 Burkhart, R., 491  
 Burkhead, P., 161  
 Burkin, 643, 650  
 Burley, F. H., 661, 669  
 Burmann, F. W., 467, 469  
 Burns, N., 262, 272, 293  
 Burns, R. F., 162  
 Burrell, J. R., 522, 533, 537, 540, 543, 544  
 Burroughs, L. C., 230  
 Burrows, (Sir) R., 37  
 Bursall, F. H., 229, 234, 417  
 Burszlyn, I., 333  
 Burt, R. B., 22, 167, 190  
 Burton, 635, 649  
 Burton, W. G., 533  
 Burwell, R. L., 160  
 Busch, J., 540  
 Bushby, S. R. M., 600, 618  
 Bushnell, 437  
 Bushrod, C. J., 143, 147  
 Buskirk, H. H., 545  
 Buss, H., 540  
 Buston, H. W., 442  
 Buswell, A. M., 665, 669  
 Butchers, E., 146  
 Butler, J. A. V., 551, 568  
 Butler, K. H., 178, 192  
 Butterfield, C. T., 654, 667  
 Butterworth, S. W., 527, 542  
 Button, J. E., 530, 542

Buxton, L. O., 253  
 Buyanov, N. V., 119  
 Buzas, A., 591  
 Byoichin, 638, 649  
 Bynum, E. K., 450

## C

Cadman, W. H., 228, 234  
 Cady, E. L., 366  
 Cady, J. G., 168, 190  
 Cady, L., 667  
 Caesar, C. H., 221, 233  
 Caesar, P. D., 358, 365  
 Cahoon, N. C., 163  
 Cairns, 649  
 Cairns, A., 513, 518  
 Cairns, D., 460, 464  
 Calbert, C. E., 668  
 Calderwood, H. N., 667  
 Caldwell, A. C., 466, 469  
 Caldwell, D. H., 658, 668  
 Caldwell, J. S., 536, 544  
 Caldwell, M. J., 544  
 Caldwell, M. R., 161  
 Calhoun, 642, 650  
 California Research Corp., 193  
 Calise, V. J., 25, 668  
 Callow, 314, 321  
 Callow, E. H., 521, 540  
 Callow, R. K., 578  
 Calvert, C. K., 667  
 Camerini, 649  
 Cameron, 441, 451  
 Cameron, A. T., 519  
 Campbell, I. E., 145  
 Campbell, M. A., 600  
 Campbell, T., 103, 124  
 Canac, F., 266, 268, 272  
 Canadian Advisory Council for Scientific & Industrial Research, 365  
 Canadian Gas Association, 61  
 Canadian Pulp and Paper Association, 327  
 Cannella, C., 522, 540  
 Canner, A. D., 163  
 Capell, A., 451  
 Capell, R. G., 23  
 Caplan, S., 386  
 Capp, J. P., 212  
 Carbide & Carbon Chem. Corp., 70, 75, 193, 250, 375, 386  
 Cardinal, E. V., 617  
 Cardon, B. P., 559, 570  
 Carey, M., 82, 94  
 Carlene, 316, 321  
 Carlinfanti, E., 526, 541  
 Carlson, G. J., 22  
 Carlson, H. M., 214  
 Carmody, W. R., 145  
 Carnahan, F. L., 20  
 Carnall, R. G., 19

Carne, J. B., 292  
 Caron, P. A., 563, 571  
 Carpenter, C. B., 166, 190  
 Carpenter, F. H., 514, 599, 617  
 Carpenter, J. E., 180, 192  
 Carpenter, L. E., 539, 545  
 Carr, R. L., 408  
 Carreker, R. P., 142, 146  
 Carroll, 644, 650  
 Carroll, 640, 642, 650  
 Carroll, W. E., 470, 545  
 Carruthers, W. R., 175, 191  
 Carter, 441, 446, 451, 452  
 Carter, G. K., 6  
 Carter, H. C., 599  
 Carter, R. H., 483  
 Carter, R. P., 82, 94  
 Carter, W. J., 163  
 Cartlidge, C., 110, 124  
 Cartwright, N. J., 619  
 Cartwright, W. F., 232  
 Case, B. C., 162  
 Casey, J. P., 496  
 Cass, W. G., 531, 542  
 Casselberry, N. H., 491  
 Cassil, C. C., 451  
 Castell, C. H., 523, 540  
 Castro, R., 118, 119, 126  
 Catch, J. R., 587, 600, 618  
 Catlin, W. E., 362, 366  
 Catlow, E., 462, 464  
 Catravas, G. N., 425, 433  
 Cattaneo, P., 254  
 Cauwenberg, W. J., 193  
 Cawley, C. M., 230, 234  
 Cazier, J., 564, 571  
 Celanese Corp. of America, 370, 375  
 Cellan-Jones, G., 58  
 Cellomold Ltd., 365  
 Chadapaux, J., 496  
 Chadwick, A. F., 364  
 Chadwick, E., 373  
 Chadwick, E. J., 395  
 Chadwick, N. E., 654, 667  
 Chaiet, L., 601  
 Chain, E., 608, 617  
 Chalin, C., 162  
 Challenger, F., 233  
 Chalmers, B., 146, 162  
 Chambard, P., 423, 433  
 Chamberlain, E. A. C., 214  
 Chamberlain, J. C., 478  
 Chamberlain, N. H., 307, 308  
 Chambers, F. S., 169, 191  
 Chambret, F., 313, 320, 362, 366  
 Champetier, G., 366, 496  
 Chance, W. H. S., 270, 273  
 Chang, L. C., 111, 125  
 Chang, S. L., 667  
 Chan Szu Shiang, 324  
 Chao-yu, C., 533, 543  
 Chapman, F., 385, 387  
 Chari, C. N., 536, 544

- Charles, A. M., 430, 434  
 Charlton, W., 364  
 Charnbury, H. B., 212  
 Charpentier, L. J., 450  
 Charrin, V., 103, 124  
 Chase, D., 293  
 Chaston, J. C., 144, 147  
 Chater, W. J., 424, 433  
 Chater, W. J. B., 433  
 Chaterjee, 312, 320  
 Chatfield, H. W., 382  
 Chaudin, R. S., 443  
 Chaudron, G., 137, 146, 162  
 Chauny, 464  
 Chechak, 648, 651  
 Cheftel, H., 538, 545  
 Chernerda, C., 542  
 Chernerda, J. M., 593  
 Chemical Construction Corp., 191  
 Chenet, M., 105, 124  
 Cheney, A. J., 9  
 Cheney, H. A., 87, 77  
 Chenioek, J. A., 233  
 Cherniavsky, A. J., 67, 77  
 Cherry-Downes, H. A. D., 549, 567  
 Cheryukov, L. D., 211  
 Chessevent, L., 291  
 Chesters, I. H., 106, 124  
 Chesters, J. H., 293  
 Cheyney, L. E., 373  
 Chiang, M.-C., 599  
 Chichelli, M. T., 10  
 Child, F. C., 134, 145  
 Childs, J. F. L., 542  
 Chilton, 644, 650  
 Chipman, W. A., 667  
 Chirnside, R. C., 264, 272  
 Chisholm, R. D., 437, 446, 452  
 Chittenden, F. D., 416  
 Chorazy, M., 212  
 Choudary, K. S., 434  
 Choudry, P. K., 369  
 Christensen, C. M., 547, 566  
 Christiansson, B., 212  
 Christie, G. J., 491  
 Christie, J. R., 479, 480  
 Christoffersen, J., 555, 569  
 Christopher, E. P., 542  
 Christopher, G. L. M., 332, 365  
 Chuiko, N. M., 120, 126  
 Chuprin, K. K., 111, 125  
 Church, H., 180, 192  
 Churchward, R. E., 161  
 Cibulskis, W. S., 123, 126  
 Cinema-Television Ltd., 194  
 Cirey, 464  
 Clapham, H., 304, 308, 321  
 Clapp, J. T., 9  
 Clark, B. S., 534, 543  
 Clark, C. B., 288  
 Clark, C. K., 621, 631, 649  
 Clark, F. E., 416  
 Clark, G. L., 289  
 Clark, M. A., 366  
 Clark, H. T., jun., 146  
 Clark, J. d'A., 334  
 Clark, J. H., 626, 632  
 Clark, K. G., 359, 365, 460, 464  
 Clark, R. A., 397, 398  
 Clark, R. N., 652, 667  
 Clark, S. P., 12  
 Clark, T. F., 364  
 Clark, W. E., 162  
 Clarke, E. P., 547, 566  
 Clarke, I. C., 434  
 Clauser, H. R., 122, 126  
 Clay, M. F., 388  
 Clappool, L. L., 530, 542  
 Clayton, C. N., 479, 480  
 Clayton, M. M., 538, 545  
 Clayton, T. L., 192  
 Cleaves, J. C., 18  
 Clegg, L., 209, 215  
 Clegg, L. F. L., 653, 667  
 Clement, A. G., 212  
 Clement, P., 373  
 Clemes, A., 145  
 Clemo, G. R., 584  
 Clendenin, J. D., 214  
 Clendenning, K. A., 497  
 Cleveland, F. C., 549, 567  
 Cleveland, F. J., 502  
 Cliffe, W. R., 176, 192  
 Clifton, S. J., 214  
 Clinton, F. L., 161  
 Cloek, R. C., 163  
 Cochran, W. C., 160  
 Cockbain, E. G., 400, 415  
 Cody, B. H., 128  
 Coes, L., 383, 386  
 Coffan, D. D., 314, 321, 362, 366  
 Coghill, R. D., 604, 616  
 Cohan, L. H., 418  
 Cohen, M., 116, 125  
 Cohen, P., 212  
 Cohen, S. G., 347  
 Coleclough, T. P., 105, 124  
 Cole, E. L., 438  
 Cole, G. M., 163  
 Coles, G., 211  
 Coles, H. W., 351  
 Colgate-Palmolive-Peet Co., 253  
 Colichman, F. L., 569  
 Colin-Russ, A., 430, 434  
 Colla, C., 559, 569  
 Collier, J. G. C., 518  
 Collins, 642, 650  
 Collins, A. A., 131, 145  
 Collins, D. L., 478  
 Collins, N., 180, 192  
 Collinson, H. A., 365  
 Collyer, P. W., 263, 272  
 Colman, E. A., 454  
 Colmer, A. R., 662, 669  
 Colombier, L., 112, 125  
 Colon, I. A., 518

- Colorado Fuel Iron Corp., 193  
 Colquhoun, J., 617  
 Colt, E. W., 253  
 Colwell, W. E., 466, 469  
 Comeford, J. E., 277  
 Comings, E. W., 9, 24  
 Commercial Solvents Corp., 191, 617  
 Commons, C. H., 269, 273  
 Commonwealth Edison Co. of Chicago,  
   203, 212  
 Comp. de Prod. Chim. et Électrométab.  
   Alais, Froges & Camargue, 193  
 Comptoir des Textiles Artif. S.A.R.L.,  
   175, 191  
 Comstock, R. L., 172, 174, 191  
 Concordia, C., 6  
 Conger, T. W., 600  
 Conn, J. B., 601  
 Connell, C. B. B., 21  
 Conner, T. J., 163  
 Conrad, 310, 320  
 Consden, R., 299, 308, 434  
 Considine, D. M., 28  
 Consolidated Mining & Smelting Co., of  
   Canada Ltd., 166, 190, 192  
 Conway, E. J., 434  
 Cook, A. H., 608, 617, 618, 619  
 Cook, J. G., 366  
 Cook, J. H., 110, 124  
 Cook, J. W., 594  
 Cook, M. H., 600  
 Cook, R. L., 293  
 Cook, R. M., 120  
 Cook, W. S., 418  
 Cooke, C., 618  
 Cooper, C., 55  
 Cooper, D. E., 617  
 Cooper, H. M., 215  
 Cooper, H. S., 180, 192  
 Cooper, L. V., 418  
 Cooper, W. F., 32  
 Cope, F. W., 5  
 Corbin, H. E., 327  
 Cori, C. F., 553, 568  
 Cori, G. T., 553, 568  
 Cormack, M. W., 469  
 Corman, J., 502, 551, 568, 570, 571  
 Cornand, P., 567  
 Cornelius, Y. R., 261, 272  
 Corning Glass Works, 366, 387  
 Corn Products Refining Co., 495  
 Corse, J., 599  
 Corse, J. W., 599  
 Cory, M. T., 205, 214  
 Cosbie, A. J. C., 560, 570  
 Cosgrove, D. J., 621, 631  
 Costa, A. F., 631, 632  
 Costa, D., 522, 540  
 Cosulich, D. B., 600  
 Cottell, G. A., 140, 146  
 Cotton, R. H., 532, 543  
 Cottrall, 314, 321  
 Cottrell, A. H., 141, 146  
 Cottrell, H. J., 547, 566  
 Cottrell, R. H., 507, 517  
 Courtaulds, Ltd., 213  
 Courtier, A. J., 166, 190  
 Cousins, E., 350  
 Cowan, A. H., 51  
 Cowan, J. C., 254  
 Cowling, J. E., 393, 417  
 Cox, C. I., 178, 192  
 Cox, E. G., 20  
 Cox, H. R., 195  
 Cox, P. E., 281  
 Cox, R. P., 382  
 Cox, S. M., 263, 265, 272  
 Crabtree, J., 412, 418, 643, 644, 650  
 Craig, A. M., 358, 365  
 Craig, L. C., 573, 577, 600, 617, 618  
 Cram, D. J., 615, 618  
 Crandall, 643, 650  
 Crane Packing Co., 7  
 Crater, W. D., 77  
 Craver, J. K., 395  
 Crawford, 651  
 Crawford, J. W., 366  
 Crawford, R., 212  
 Crawshaw, H. A., 491  
 Creamer, A. S., 292  
 Cree, J. C., 227, 234  
 Crentz, W. L., 198, 212  
 Crichton, A. B., 38, 196, 211  
 Crighton, J. T., 450  
 Cristy, G. A., 365  
 Crocker, C., 478  
 Crombie, A. C., 482, 483  
 Cromer, H. W., 174, 191  
 Crook, 317, 321  
 Crook, A. E., 212  
 Cross, H. E., 145  
 Crossland, J., 211  
 Crossland, L. B., 500  
 Crossley, H. E., 27, 204, 214  
 Crowe, G. R., 555, 569  
 Crowther, E. M., 461, 464, 465, 469  
 Cruess, W. V., 531, 535, 536, 543, 544  
 Crystol, S. J., 586  
 Cservenyak, F. J., 184, 193  
 Ctyroky, V., 269, 273  
 Cüer, 636, 649  
 Cuff, C. M., 560, 570  
 Cuillaumeron, P., 164, 190  
 Cullinane, N. M., 364  
 Cullom, W. F., 371  
 Culpepper, C. W., 535, 544  
 Cumming, W. M., 20, 31  
 Cummings, A. D., 64  
 Cummings, W. H., 434  
 Cunccliffe, W., 528, 542  
 Cunneen, J. I., 417  
 Cunningham, G. E., 423, 424, 433  
 Cunningham, G. L., 176, 192  
 Cunningham, W. K., 185, 193  
 Curd, F. H. S., 491, 509  
 Curl, A. L., 532, 543

Curtis, C. E., 293  
 Curtis, F. J., 366  
 Curtis, L. C., 254  
 Cusick, C. F., 28  
 Cuthbert, F. L., 293  
 Cuthbertson, J. W., 162  
 Czorwin, E. P., 362, 366

## D

Dabney, H. L., 668  
 Daglish, C., 537, 544  
 Dahlberg, 541  
 Dahle, F. B., 163  
 Dale, A. E., 268, 272  
 Dale, J. J., 162  
 Dalfsen, J. W. van, 415  
 Dalglish, C. E., 295, 308  
 Dalton, L. K., 364  
 Dammers, H. F., 219, 230, 233, 234  
 Danby, C. J., 348  
 Dance, J. B., 161  
 Dange, G. V., 178, 192  
 Daniels, F., 11  
 Daniels, H. S., 327, 669  
 Danielson, R., 330  
 Danielsson, C., 103, 124  
 Danielsson, C. E., 551, 568  
 Dammernberg, E. M., 417  
 D'Arquin, E. L., 416  
 D'Argila, M., 622, 631  
 Darmois, E., 264, 272  
 Darmon, S. E., 295, 308  
 Darrow, G. M., 545  
 Das, R. K., 212  
 Daubert, B. F., 254, 539, 541, 545  
 Daubert, W. S., 511, 517, 518  
 Daudt, W. H., 366, 387  
 Daughenbaugh, P. J., 491  
 Davey, 642, 650  
 Davey, D. G., 599  
 Davey, J. G., 491  
 Davey, W. S., 400, 415  
 D'Avice, R., 504, 516  
 David, W. A. L., 478  
 Davidson, 311, 321  
 Davidson, J., 466, 469  
 Davies, C., 476, 478  
 Davies, C. W., 358, 365  
 Davies, D. N., 365  
 Davies, D. T., 190, 198, 212  
 Davies, J. G., 505, 516, 517  
 Davies, J. K., 144, 147  
 Davies, W., 291, 465, 469  
 Davis, A. G., 466, 469  
 Davis, J. G., 524, 541, 555, 569  
 Davis, L. P., 161  
 Davis, R. F., 203, 213  
 Davis, W. C., 364  
 Davison Chem. Corp., 193  
 Dawe, A., 211  
 Dawson, T. R., 408

Day, H. M., 25  
 Day, R. S., 10  
 Day, T. D., 421, 433  
 Dayrit, C., 602  
 Dayton, B. B., 18  
 Dazeley, G. H., 227, 234  
 De Almeida, J. R., 516, 518  
 Dean, F. P., 451  
 Deanin, R., 417  
 Dearden, J., 120, 125  
 Dearing, W. C., 365  
 Deartherage, F. E., 521, 540  
 De Ascona, J. M. L., 212  
 De Bach, P., 451  
 Debenham, W. S., 106, 124  
 Debing, L., 357, 364  
 Debot, 635, 649  
 De Bruyne, N. A., 270, 273, 365  
 De Chanville, J. H., 266, 272  
 De Cholnoky, L., 517  
 De Clerck, J., 546, 564, 571  
 De Dominico, G. B. R., 437  
 De Dominico, M., 437  
 Dee, C. E., 491  
 Deegan, C. J., 233  
 De Groot, P. W., 500  
 Degruy, I. V., 416  
 Deitz, V. R., 9, 517  
 De Jong, W., 381, 382  
 De Keyser, W., 293  
 Dekker, C. A., 587  
 De Lamothe, G. F., 541  
 Delaporte, 518  
 Delassus, M., 201, 213  
 De la Vea, G. A. K., 518  
 Delisle, 445, 452  
 Delmonte, J., 364, 371  
 De Long, H. K., 161  
 Delor, R. A., 545  
 Delorme, J., 343  
 Demart, P., 61  
 De Martini, F. E., 662, 669  
 Demassieux, N., 103, 124  
 De Ment, J., 292  
 Demer, L. J., 136, 146  
 Demerec, M., 616  
 Demidenko, T. T., 470  
 De Mingo, M., 254  
 Demorest, D. J., 212  
 Dempsey, M., 433, 434  
 Dempsey, T. G., 588  
 Denman, W. L., 10  
 Denning, P. S., 192  
 Dennis, W., 192  
 De Nora, V., 163, 183, 193  
 Dent, F. J., 59  
 Denzler, C. G., 14  
 De Ong, E. R., 478  
 Derby, R. I., 542  
 Dérivé, M., 547, 567  
 De Ritter, E., 544  
 De Sa, J., 598  
 Desalbres, L., 451, 632

- Deschreider, A. R., 544  
 Deshusses, J., 631, 632  
 Desnuelle, P., 253, 381  
 Despaul, J. E., 570  
 Dessus, M. G., 195, 211  
 De Sy, A., 162  
 Desyatnikov, O. G., 161  
 Detwiler, I. G., 230  
 Deuel, H. J., 544  
 Deutschman, A., 117  
 Deutsch, F. S., 365  
 Deux, Y., 570  
 Devaux, R., 201, 213  
 Devi, P., 537, 544  
 De Vries, J., 264, 272  
 De Vries, W. H., 599  
 De Wael, J., 483  
 De Walt, C. W., 576  
 Dewar, E. T., 550, 567, 583  
 De Whalley, H. C. S., 513, 518  
 De Wilde, R., 563, 571  
 De Willegen, A. H. A., 500  
 De Witt, E. G., 77  
 Dexter, F. D., 394, 395  
 Dexter, S. T., 466, 469  
 Dey, B. B., 79  
 D'Herron, R. L., 146  
 Diamond, J. J., 264, 272  
 Dickie, H. A., 112, 125  
 Dickinson, 640, 650  
 Dickson, A. D., 551, 564, 567, 571  
 Dickson, J. T., 361, 366  
 Diennair, W., 537, 544  
 Dienes, G. J., 394, 395  
 Diesel Engine Users Assoc., 161  
 Dietz, H. J., 194  
 Dietzel, A., 257, 271  
 Digges, T. G., 115, 125  
 Dijkhuis, J. G., 324  
 Diller, H., 538, 545  
 Dimant, E., 597  
 Dimsdale, 639, 650  
 Dinger, K., 260, 268, 272  
 Dinsmore, R. P., 417  
 Di Pietro, W. O., 133, 145  
 Dippel, 648, 651  
 Distelborst, S. D., 25  
 Distillation Products Inc., 254  
 Distillers Co., 66, 70, 77  
 Ditcham, J. B., 229, 234, 117  
 Dittner, K., 586  
 Dittrich, C. W., 167, 190  
 Divekar, P. V., 598  
 Dixon, D., 293  
 Dixon, J. K., 332, 365  
 Dlouhy, J. E., 502  
 Dobbins, 645, 650  
 Dodge, B. F., 8, 181, 192  
 Doebel, K., 590  
 Döhler, L., 162  
 Doehner, K., 525, 541  
 Doherty, 427, 434  
 Dolah, R. W. van, 629, 632  
 Dolder, van der, 648, 651  
 Dole, 447, 452  
 Dole, M., 308  
 Dollear, F. G., 254, 541  
 Dolliver, M. A., 575, 617  
 Dolton, R. H., 563, 571  
 Domagk, G., 569  
 Domingo, C. E., 454  
 Dominion Magnesium Ltd., 192  
 Donelson, E. G., 472  
 Donnison, G. H., 503  
 Donovick, R., 618  
 Doolittle, A. K., 372  
 Doolittle, S. P., 480  
 Dorey, S. F., 32  
 Dorfman, A., 553, 568  
 Doss, 504  
 Doty, 319, 321  
 Dougill, D., 53  
 Douglas, A. A., 517  
 Doull, J., 450  
 Dove, H. C., 545  
 Dove, W. E., 450  
 Do Vale, J. C., 631, 632  
 Dow Chemical Co., 66, 67, 153, 341, 366, 451  
 Dowd, J. J., 212  
 Downham, K. O., 491  
 Downie, C. C., 21, 29  
 Downs, G. R., 59  
 Doyle, D. E., 230, 234  
 Drake, C. F., 393  
 Drake, M., 474  
 Drake, S. S., 417  
 Dregne, H. E., 469, 474  
 Drennen, T. J., 569  
 Dreyer, J. F., 270, 273  
 Dreyfus, H., 375  
 Driessche, S. van den, 536, 544  
 Drotschmann, C., 163  
 Dryden, J. S., 292  
 Dubeau, A. L., 300, 307  
 Du Bois, A. S., 569  
 Du Bois, K. P., 450  
 Dubpernell, G., 161  
 Dubrul, L., 185, 193, 261, 272  
 Duchon, K., 332, 653, 667  
 Dudding, 261  
 Dudzinski, N., 140, 146  
 Duffy, T. H., 210, 215  
 Dufrenoy, J., 473, 538, 545, 617  
 Dufton, R. F., 206, 214  
 Dugan, L. R., 253  
 Dulaney, E. L., 617  
 Duley, F. L., 454  
 Dulhunty, J. A., 210, 215  
 Dulon, R., 632  
 Dumbleton, L. J., 451  
 Dunker, C. F., 543  
 Dunkley, W. H., 200, 213  
 Dunlop, S. G., 545  
 Dunn, G., 578  
 Dunn, H. C., 254

Dunn, W. E., 7  
 Dunningham, A. C., 60, 203, 212, 213  
 Dunstan, A. E., 223, 233, 234  
 Dunstan, E. J., 222, 233  
 Dupas, M. R., 228, 234  
 Dupont, G., 416  
 Du Pont de Nemours & Co., E. I., 67,  
 69, 70, 71, 72, 75, 77, 83, 85, 86, 87,  
 91, 92, 93, 96, 97, 106, 190, 191, 364,  
 365, 366, 375, 385, 649  
 Durr, 382  
 Durrer, R., 103, 124  
 Dushman, S., 15  
 Dutall, R. B., 73  
 Dutch, M., 342  
 Dutcher, J. D., 619  
 Dutron, D., 291  
 Dutt, K. B., 632  
 Dutt, S., 254, 631, 632  
 Dutton, H. J., 254  
 Du Vigneaud, V., 574, 599, 610, 617  
 Dybdal, E. C., 340  
 Dyer, B., 483  
 Dyer, F. E., 523, 540  
 Dyer, W. J., 523, 540, 541  
 Dymond, A. W. J., 232  
 Dyson, W. H., 190

## E

Eagle, H., 618  
 Eakin, R. E., 581, 582  
 Earl, J. A., 292  
 Early, E. B., 473  
 Earnshaw, F., 467, 469  
 Eastcott, A. R., 209, 215  
 Eastman Kodak Co., 69, 74, 87, 88, 89,  
 90, 92, 97, 189, 194, 375  
 Eastwood, J., 307  
 Eastwood, L. W., 133, 145  
 Ebert, A. A., 398  
 Ebert, R. H., 588  
 Eberwein, A., 542  
 Eby, L. T., 411, 418  
 Eccleston, 447, 449, 452  
 Eckard, J. W., 212  
 Eckardt, W., 162  
 Eckey, E. W., 253, 541  
 Eddiger, R. T., 212  
 Ede, A. J., 535, 544  
 Edge, J. V., 330  
 Edge, S. R. H., 501  
 Edgerton, 645, 651  
 Edgerton, L. J., 471, 472  
 Edgerton, R. O., 600  
 Edgson, F. A., 491  
 Edinger, J. C., 214  
 Edmondson, J. H., 660, 668  
 Edneral, T. B., 118, 126  
 Edwal Laboratories, Inc., 74  
 Edward, J., 209, 215  
 Edwards, A. H., 210, 215  
 Edwards, D. A., 10  
 Edwards, D. G., 24  
 Edwards, E. G., 366  
 Edwards, F. E., 464  
 Edwards, J. P., 599  
 Edwards, L. J., 255  
 Edwards, S. J., 491  
 Edwards, W., 212  
 Efanov, N. I., 109, 124  
 Efron, A., 502, 567  
 Egartner, L., 162  
 Egerton, G. S., 304, 308, 318, 321  
 Eggert, 640, 650  
 Egginton, H. H., 162  
 Egloff, G., 217, 218, 222, 232, 233  
 Ehinger, R., 545  
 Ehrenberg, P., 545  
 Ehrlich, J., 572, 577, 618  
 Eichhorn, J., 25  
 Eigel, G., 541  
 Eigen, E., 576  
 Ellender, W., 116, 125, 161  
 Eisenberg, A. A., 10  
 Eisenklam, P., 215  
 Ekman, E., 212  
 Elder, J. L., 212  
 Elder, L. W., 254  
 Eldridge, E. F., 666, 669  
 Electrolytic Manganese Corp., 153  
 Eley, D. D., 356, 364  
 Elford, H. S., 196, 211  
 Ellenberger, H. A., 543  
 Ellenger, H. C., 292  
 Elliot, M. A., 166, 190  
 Elliot, R., 412, 418  
 Elliott, D. F., 586  
 Elliott, E., 118  
 Elliott, R. P., 523, 540, 541  
 Ellis, D. E., 479, 480  
 Ellis, D. G., 161  
 Ellis, J. W., 302, 308  
 Ellis, M. M., 667, 669  
 Ellis, S. G., 223, 233  
 Ellison, H. E., 517, 518  
 Ellison, R. J., 669  
 Elsd, E., 297, 298, 307, 308, 313, 320  
 Elsea, A. R., 146  
 Elsner, B. B., 233  
 Flassner, G., 160  
 Elsworth, F. F., 308  
 Eltenton, G. C., 224, 233  
 Elvehjem, C. A., 543, 544, 568  
 Elvidge, J. A., 619  
 Elvidge, W. F., 537, 544  
 Elving, P. J., 398, 570  
 Elzi, F. A., 193  
 Emblem, H. G., 293, 385, 387  
 Emel us, H. J., 271, 273, 366  
 Emery, W. B., 618  
 Emery Industries Inc., 253, 381  
 Emmett, A. D., 545  
 Endell, K., 292, 293  
 Engblom, A., 500

Engdahl, R. B., 214  
 Engel, A., 146  
 Engeler, A., 299, 308  
 Engle, J. B., 667  
 Entwistle, K. M., 140, 146  
 Epelboim, I., 162  
 Epremian, E., 115, 125  
 Epstein, R., 213  
 Epstein, S. S., 565, 571  
 Epton, S. R., 255  
 Erb, C., 509, 517  
 Erdmann, R., 163  
 Erganian, G., 669  
 Erickson, A. B., 451  
 Erickson, L. C., 466, 469  
 Erlenmeyer, H., 588  
 Ernsberger, F. M., 426, 434  
 Ernst, A. J., 323  
 Ertel, C. W., 270, 273  
 Esmarch, W., 133, 145  
 Espenmiller, H. P., 330  
 Esselbaugh, N. C., 544  
 Esselin, W. B., 542  
 Esselen, W. B., jun., 543  
 Estartus, F. G., 366  
 Etgen, E., 618  
 Ettinger, M. B., 668  
 Eugster, C. H., 585  
 Euler, H. von, 364  
 Euw, J. von, 591  
 Evans, C. A., 482, 483  
 Evans, H., 512, 518  
 Evans, N. L., 162  
 Evans, R. E., 486, 488, 539, 545  
 Evans, U. R., 114, 125  
 Evans, V., 29  
 Evans, W. M., 491  
 Everett, H. J., 34  
 Ewart, R. H., 348  
 Ewing, D. T., 161, 538, 545  
 Ewing, J. R., 162  
 Ezell, B. D., 538, 544, 545

## F

Fahrenbach, M. J., 600  
 Fahrenwald, A. W., 127, 144  
 Fair, G. M., 667  
 Fairbairn, A. W., 67, 77  
 Fairbanks, B. W., 528, 542  
 Fairfield, R. G., 222, 233  
 Fairs, G. L., 19  
 Fajans, E., 478  
 Fajans, K., 256, 271  
 Falcon, N. L., 211  
 Fales, J. H., 437, 450, 451  
 Falk, L. L., 658, 668  
 Falkenburg, L. B., 254, 381, 382  
 Falla, 649  
 Fallesen, 642, 644, 650  
 Fan, H. P., 12  
 Fancutt, F., 417

Fanderlik, M., 268, 273  
 Faraday Society, 127, 129  
 Farander Garcia, R., 518  
 Farber, E. A., 10  
 Fardig, O. B., 543  
 Farina, R. L. J., 365  
 Farnworth, A. J., 299, 308  
 Farr, H., 381  
 Farrell, 647, 651  
 Fassina, L., 53  
 Fastovsky, V. G., 182, 193  
 Faust, C. L., 162, 163  
 Favor, H. H., 500, 529, 542  
 Fawcett, E. W. M., 16  
 Fay, R. W., 438  
 Fayette, L. J., 451  
 Feaster, J. F., 543  
 Febbraro, E., 544  
 Federal Telephone & Radio Corp., 193  
 Fehling, H. R., 202, 213  
 Feichtinger, H., 223, 233  
 Felicetta, V. F., 328  
 Felix, W. R., 203, 212, 213  
 Fellenberg, T. von, 528, 542  
 Fellers, C. R., 542, 543  
 Fellows, J. R., 215  
 Felsner, O., 213  
 Felton, J. R., 212  
 Fenske, M. R., 224, 233  
 Fenton, F., 544  
 Fenton, G., 110, 124  
 Ferguson, G. W., 629  
 Ferguson, R. R., 329  
 Ferguson, W. S., 487, 488  
 Ferlan, M., 499  
 Fern, 316, 321  
 Fernandes, F., 598  
 Fernandez, R. R., 518  
 Ferrari, C. G., 542  
 Ferri, V., 109, 124  
 Fertiliser Society, 459  
 Fidell, 304, 308  
 Fidler, J. C., 529, 542  
 Field, B. R., 163  
 Field Information Agency, 160  
 Fielding, J. H., 417  
 Fielmann, W., 545  
 Figgat, W. B., 669  
 Fillman, J., 586  
 Filmer, 648, 651  
 Finch, R. B., 432, 434  
 Fineman, M. N., 382  
 Finger, J., 261, 272  
 Fingerling, G., 487, 488  
 Finholt, R. W., 340  
 Fink, W. L., 138, 146  
 Finland, M., 576, 618  
 Finlayson, T. C., 46, 208, 215  
 Finlayson, W. H., 214  
 Finnegan, T. J., 210, 215  
 Finnegan, W. J., 536, 544  
 Finney, D. J., 436, 534, 543  
 Firestone Tyre & Rubber Co., 73

- Firth, L. F., 25  
 Fischer, E. K., 405, 416, 500  
 Fischer, L., 621, 631  
 Fischer, O., 524, 541  
 Fischer, R. B., 277, 292  
 Fishburn, B. B., 586  
 Fisher, C. H., 346, 417  
 Fisher, D. V., 530, 542  
 Fisher, G. S., 254, 541  
 Fisher, P. D., 168, 190  
 Fishwick, 315, 316, 321  
 Fitzgerald, R. J., 576  
 Fitzgerald, T. H., 418  
 Fitzwilliam, C. W., 506, 516  
 Flanagan, T. L., 569  
 Fleck, E. E., 483  
 Fleisch, C. J., 293  
 Fleischanderl, J., 538, 545  
 Fleming, 319, 321, 446, 452  
 Fletcher, H. L., 480  
 Fleurquin, M. P., 195, 211  
 Floe, C. F., 162  
 Flood, A. C., 517  
 Flor, H. H., 467, 469  
 Floro, M. B., 516, 518  
 Florey, (Sir) H., 603  
 Flory, P. J., 361, 366, 418  
 Flösdorf, E. W., 22  
 Fluke, D., 18  
 Fluno, H. G., 444  
 Flynn, E. H., 599  
 Foëx, M., 135, 145, 260, 272  
 Fogg, G. E., 438  
 Fogler, B. B., 31, 181, 192  
 Folkers, K., 575, 576, 582, 599, 601  
 Fonseca, E. de C., 622, 631  
 Fontana, M. G., 120, 125  
 Fookson, A., 222, 233  
 Foote, F. J., 480  
 Forbes, E. J., 233  
 Ford, 8  
 Ford, J. H., 578, 599  
 Ford, O. W., 481, 483  
 Ford, W. F., 285, 293  
 Forest Research Institute, Dehra Dun,  
 324  
 Forman, C. R., 491  
 Formo, J., 364  
 Forrest, H. S., 581  
 Forrest, J. W., 269, 273  
 Forrester, C., 213  
 Forsyth, W. G. C., 212  
 Foster, A. L., 233  
 Foster, A. W., 28  
 Foster, J. F., 61  
 Foster, J. W., 616  
 Foter, M. J., 569  
 Found, G. H., 146  
 Fourness, 318, 321  
 Fourt, 319, 321  
 Fowler, 649  
 Fox, E. J., 168, 190  
 Fox, F. A., 144, 147  
 Fox, K., 133, 145  
 Fox, K. M., 417  
 Foxwell, G. E., 45, 49, 64  
 Francis, 234  
 Fraenkel-Conrat, H., 308  
 Fränz, I., 542  
 France, W. G., 426, 434  
 Francis, J., 491  
 Francis, M., 290  
 Frank, F. C., 142, 146  
 Frank, J. F., 491  
 Frank, R. L., 417  
 Franklin, J. N., 28  
 Frary, F. C., 160  
 Frary, G. C., 524, 541  
 Fraser, D. A., 365  
 Fraser, G. K., 197, 211, 212  
 Fraser, R., 330  
 Fraser, T., 198, 212  
 Frattali, F. J., 184, 193  
 Frazer, E. H., 212  
 Frazier, P. M., 214  
 Freak, M. J., 491  
 Froar, D. E. H., 436  
 Freed, B., 510, 517  
 Freeman, G. G., 566, 571  
 Freeman, S. M., 416  
 Freilich, J., 542  
 Freiman, M. J., 596  
 French, D., 528, 542  
 Frenkel, 634, 649  
 Fresenius, W., 537, 544  
 Freudenberg, K., 550, 567  
 Frey, C. N., 556, 569  
 Frey, F. E., 225, 234  
 Fricke, E. F., 467, 469  
 Fried, J., 576, 618  
 Fried, J. F., 540  
 Friedberg, A. L., 292  
 Friedman, 647, 651  
 Friedman, R., 618  
 Friedman, S., 212  
 Friedman, S. J., 9  
 Friedman, V. M., 191  
 Friedmann, D., 364  
 Frillette, V. J., 341  
 Frillette, 309, 310, 320  
 Frith, G. R., 667  
 Fröhlich, 651  
 Frölich, J., 356, 364  
 Fromm, 316, 321  
 Fruton, J. S., 587  
 Fry, 639, 650, 651  
 Fry, D. J., 83  
 Fryling, C. F., 417  
 Fuhrmann, A., 418  
 Fukas, G., 493  
 Fuld, M., 497  
 Fulda, W., 193  
 Fuller, A. H., 657, 668  
 Fuller, C. F. H., 501  
 Fullmer, F. S., 463, 464  
 Fulmer, E. I., 565, 571

Fulton, R. A., 437, 439

Funk, C. R., 111, 125

Furnas, 8

Gaddy, V. L., 463, 464

Gaffert, H., 545

Gagliardi, 319, 321

Gakhokidge, A. M., 344

Gale, E. F., 555, 569, 607, 617

Gall, D., 227, 234

Gallacher, G. G., 28

Gallagent, 651

Gallagher, E. C., 381

Gallay, W., 254

Galstoffs, P. S., 667

Gambhir, I. R., 254

Gane, R., 530, 532, 542, 543

Gapuz, D. B., 431, 434

Gardner, E. G., 42

Gardner, G. D., 185, 193

Garion, M., 517

Garland, J., 145

Garlick, G. F. J., 188, 194

Garnor, E. V., 303, 308

Garner, F. H., 228, 234

Garrett, S. D., 469

Garrison, L., 599

Garside, J. E., 20, 52

Garton, F. W., 112

Gas Light &amp; Coke Co., Ltd., 191, 193

Gas Research Board, 58, 62

Gaskins, W. W., 277, 292

Gastel, L. A. van, 563, 571

Gates, R. L., 551, 568

Gaylor, P. J., 510, 517

Gazzola, A. L., 601

Gearhart, W. M., 395

Gebauer, K., 161

Gee, E. A., 185, 193

Geer, M. R., 212

Gehm, H. W., 665, 669

Gehman, S. D., 412, 418

Geigel, M., 113, 125

Geiger, A., 600

Geiger, C. F., 293

Geigy, J. R., 75

Geigy, Akt.-Ges., J. R., 76, 83, 84, 85, 86

Geigy Co., 365

Gelman, M. M., 291

Gemas, M., 69

Gemeinhardt, K., 538, 546

Gemmell, D. C. N., 214

Genda, 649

Gen. Aniline &amp; Film Corp., 75, 76, 83, 98

Gen. Chemical Co., 191

Gen. Electric Co., Ltd., 188, 194, 364, 366

Gen. Foods Corp., 254

Gen. Motor Corp., 375

Gen. Printing Ink Corp., 74, 93

Genevois, L., 538, 545

Gentry, 264

Gentry, C. H. R., 162

George, F., 293

George, T. K., 659, 668

Georges, P., 42

Georgian, C. C., 12, 253, 381

Gericke, S., 468, 470

Gerivo, R. D., 542

German, H. L., 485, 487

German, M. Y., 213

Gerould, 643, 650

Gersdorff, W. A., 450

Gerstenmaier, J., 419

Gertsen, H. C., 214

Getty, R. L., 505, 516

Geukenne, A., 212

Ghosh, D. N., 505, 516

Ghosh, J. C., 233

Ghosh, N. C., 545

Ghosh, S. C., 56

Gibbons, N. E., 527, 535, 541, 542, 543, 544

Gibson, H. B., 233

Gibson, M., 665, 669

Gibson, R. J., 18

Giddens, J. E., 368

Giella, M., 587

Gieselers, 201

Gifford, R., 491

Gilbert, 316, 321

Gilbert, H. L., 145

Gilbert, N., 11

Gilbert, V. E., 508, 517

Gilbert, W. E., 667

Gilder, R. D. van, 213

Gill, E. F., 207, 214

Gill, J. O., 491

Gillam, N. W., 308

Gillet, A., 198, 212

Gillis, M. B., 484, 485, 487

Gillman, H. H., 416

Gilman, H., 68, 77, 396, 397

Gillod, J., 266, 272

Gils, G. E. van, 401, 415, 416

Giral, F., 254

Givaudan &amp; Co., L., 622, 631

Gjesmoe, F., 261, 272

Gladding, J. T., 600

Glahn, von, 648, 651

Glasgow, G. U., 416

Glasgow, R. D., 439, 478

Glass, H. M., 286

Glathart, J. L., 265, 266, 272

Glatt, L., 302, 308

Glaxo Labs. Ltd., 617

Glaze, F. W., 270, 273

Glebov, S. V., 293

Gleim, E., 544

Glenn, R. A., 199, 212

- Glizmanenko, D. L., 182, 193  
 Gloster, A. J., 169, 191  
 Glover, R. E., 578  
 Gloyer, S. W., 12, 253, 381  
 Gluckert, F. A., 9  
 Glynn, E., 225, 234  
 Gocar, M., 558, 569  
 Godbole, N. N., 254  
 Godchaux, L., 519  
 Godfrey, E., 19  
 Goedkoop, W., 567  
 Goemov, V. P., 631  
 Goepfert, W. F., 518  
 Goepf, R. M., jun., 516, 519  
 Goering, H. L., 586  
 Goethe, 438  
 Goetchius, G. R., 569  
 Goglia, M. J., 24  
 Gold, H., 602  
 Goldacre, R. J., 555, 568  
 Goldberg, B., 162  
 Goldberg, H., 161  
 Golden, J. J., 286  
 Goldenberg, L. G., 175, 191  
 Goldenberg, N., 501  
 Goldfinger, G., 340  
 Goldman, K. M., 111, 125  
 Goldstein, A., 442  
 Goldstein, R. F., 218, 233  
 Goldthorpe, H. H., 660, 668  
 Gonzalez Mais, J. C., 517  
 Goodacre, C. L., 588  
 Goodall, 318, 321  
 Goodall, R. R., 607, 617  
 Gooden, 451  
 Goodlow, R. J., 618  
 Goodrich, S. R., 660, 668  
 Goodrich Co., B. F., 350  
 Goodwin, L. G., 491  
 Goodyear Tyre & Rubber Co., 416  
 Goppel, J. M., 417  
 Gorbach, G., 538, 545  
 Gordon, A. H., 299, 308  
 Gordon, D. R., 547  
 Gordon, E., 133, 145, 253  
 Gordon, H., 568  
 Gordon, K., 229, 231, 234  
 Gordon, M., 581  
 Gordon, W. D., 161  
 Gore, H. C., 531, 543  
 Gorham, P. R., 543  
 Gortner, W. A., 536, 544  
 Goss, W. H., 381  
 Gosselin, A., 201, 213  
 Gotaas, H. B., 657, 668  
 Gottlieb, D., 577  
 Gough, 445, 451  
 Gould, C. E., 261, 262, 272  
 Gourlay, J. S., 16  
 Govaert, F., 548, 567  
 Gowans, K. D., 480  
 Goy, G., 562, 570  
 Goy, O., 325  
 Goyco, J. A., 538, 545, 558, 569  
 Graber, W. P., 595  
 Gray, L., 144, 147  
 Graham, 316, 321  
 Graham, 587  
 Graham, A. K., 161  
 Graham, C. L., 194  
 Graham, E. R., 482, 483  
 Graham, J. J., 171, 191  
 Grainger, J., 467, 469  
 Gralén, N., 296, 308, 320  
 Grambow, D. A., 472  
 Grammaticakis, M. P., 83, 94  
 Grant, C. A., 254, 541, 543  
 Grant, R., 479, 480  
 Grant, W. M., 570  
 Grassie, N., 349  
 Grau, R., 521, 540  
 Grauer, O. H., 270, 273  
 Gray, 504  
 Gray, C. J., 27  
 Gray, P. P., 564, 571  
 Grayson, 441, 451  
 Greaves, J. E., 466, 469  
 Greaves, J. H., 381  
 Greaves, R. L., 52  
 Grebinsky, S. O., 464  
 Green, 437  
 Green, A. A., 553, 568  
 Green, D. E., 568  
 Green, G. H., 501  
 Green, H., 395  
 Green, J., 656, 668  
 Green, R. L., 268, 272  
 Green, S. J., 184, 192  
 Greenfield, S. H., 14  
 Greenhalgh, S. G., 21  
 Greenhill, E. B., 227, 234  
 Greenspan, F. P., 187, 194  
 Greenstreet, O. P., 542  
 Greenwell, G. H., 195, 211  
 Gregg, A. W., 107, 124  
 Gregor, M., 190  
 Gregory, J. D., 600, 618  
 Gregory, J. N., 227, 234  
 Gresham, T. L., 344  
 Gresham, W. B., jun., 450  
 Grey, C. G., 491  
 Grey, J. T., 364  
 Gridgeman, N. T., 32  
 Griebel, C., 545  
 Griess, J. C., 161  
 Griffin, C. C., 133, 145  
 Griffith, R. H., 55, 191, 193  
 Grignon, H., 571  
 Grim, J. M., 384, 386  
 Grim, R. E., 289  
 Grindley, D. N., 254  
 Grinten, van der, 651  
 Grisenthwaite, A. T., 182, 193  
 Grizzard, A. L., 469  
 Grob, C. A., 594  
 Grodzinski, P., 364

- Grof, F., 617  
 Gross, B., 412, 418  
 Gross, C. E., 543  
 Gross, C. R., 472  
 Gross, H. H., 12  
 Gross, J., 420, 433  
 Grossfeld, J., 497  
 Grossi, F. X., 579, 600  
 Grover, D. W., 537, 544  
 Grover, H. J., 146  
 Gruenwald, L. A., 365, 384, 386  
 Gruhzit, O. M., 572, 577  
 Grumell, E. S., 62  
 Grummer, M., 6, 8  
 Grunberg, L., 225, 234  
 Guenther, E., 620, 631  
 Guerrant, N. B., 543  
 Gurtler, P., 501  
 Guha, S. R. D., 233  
 Guilbeau, W. F., 416  
 Guillion, J., 451  
 Guilmart, (Mme.) T., 82, 94  
 Guinness, Son and Co., Ltd., A., 562, 570  
 Guitton, L., 122, 126  
 Guittonneau, G., 541  
 Gulate, K. C., 632  
 Gulbransen, E. A., 147  
 Gulf Research & Development Co., 73, 364  
 Gunz, W., 204, 213, 214  
 Gunderson, L. O., 10, 27  
 Gunn, J. L., 477, 478  
 Gunness, R. C., 229, 234  
 Gunsalus, I. C., 568  
 Gunther, F. A., 441  
 Gurbaxani, M. L., 668  
 Gurney, C., 266, 272, 346, 633, 649  
 Gururaja Doss, K. S., 5, 6  
 Gustavson, K. H., 422, 424, 427, 433, 434  
 Guthmann, R., 205, 214  
 Guthrie, J. D., 253  
 Gyllensvärd, E., 567
- H
- H.M. Stationery Office, 211  
 Haag, G., 545  
 Haaren, F. W. J. van, 483  
 Haas, F. J., 567  
 Habraschka, B., 386  
 Habrie, 310, 320  
 Hachmuth, K., 221, 233  
 Hackerman, N., 122, 126  
 Hadaway, A. B., 438  
 Hadden, S. T., 14  
 Hadorn, H., 531, 543  
 Haefele, C. R., 331  
 Haefele, J. W., 416  
 Häig, 636, 649  
 Haemers, H., 162  
 Haff, 647, 651  
 Hageman, R. H., 457, 467, 469  
 Hahn, E., 328  
 Hahner, C. H., 270, 273  
 Haines, W. J., 599  
 Halawani, A., 451, 598  
 Halden, W., 538, 545  
 Hale, M. G., 568  
 Hales, K. C., 535, 544  
 Halfawy, M., 162  
 Hall, A. S., 6  
 Hall, C. C., 227, 234  
 Hall, F. P., 258, 271  
 Hall, J. R., 110, 124  
 Hall, L. A., 501  
 Hall, M. W., 14  
 Hall, R. H., 431, 434, 435  
 Hall, T. A., 23  
 Halla, F., 162  
 Halle, R., 261  
 Haller, 451  
 Halliday, D. J., 461, 464  
 Halliday, E. G., 540, 543  
 Halliday, J. M. D., 106, 124  
 Halliday, M. D., 293  
 Hallsworth, E. G., 473  
 Halm, L., 179, 192  
 Halpern, A., 630, 632  
 Halsall, T. G., 498  
 Halstead, H. L., 209, 215  
 Halvorson, H. O., 534, 536, 543, 544  
 Hamaker, J., 210, 215  
 Hamence, J. H., 483  
 Hamer, 641, 650  
 Hamer, P., 25  
 Hamer, W. J., 163, 500  
 Hamilton, E. H., 270, 273  
 Hamilton, G. B., 12  
 Hamilton, T. S., 488  
 Hamm, G. G. H., 405, 416  
 Hammerstein, F. J., 502  
 Hammond, A. R., 70  
 Hammond, R. A. F., 161  
 Hamons, J. G., 464  
 Hampe, P., 478  
 Hampel, C. A., 173, 191  
 Hanby, W. E., 308  
 Handford, 645, 651  
 Handke, D. P., 381  
 Hanford, W. E., 362, 366  
 Hankins, G. A., 5  
 Hankinson, L. E., 26  
 Hanley, 295  
 Hannan, M. L., 544, 571  
 Hannan, W. S., jun., 127, 144  
 Hannaway, G. S., 323  
 Hansberry, R., 442  
 Hansen, A., 546, 556  
 Hansen, D. W., 495  
 Hansen, M. E., 403, 416  
 Hansen, W. C., 177, 192  
 Hansens, M., 548, 567  
 Hanson, 314, 317, 321

- Hanson, 647, 651  
 Hanson, G. H., 221, 233  
 Hanson, R., 599  
 Happel, J., 171, 191  
 Harbaschka, B., 364  
 Harbert, W. D., 15  
 Harbison, L., 417  
 Harborth, G., 345  
 Hardesty, J. O., 464, 481, 483  
 Harding, A. C., 178, 192  
 Harding, H. G. W., 269, 273  
 Harding, P. L., 531, 539, 542, 545  
 Harding, W. M., 582  
 Hardy, D. V. N., 361, 363, 366  
 Hargleroad, J. C., 324  
 Harley, C. P., 472, 483  
 Harley, F. H., 160  
 Harman, C. G., 291  
 Harmer, P. M., 456, 457, 467, 469  
 Harmon, R. E., 417  
 Harrington, T. M., 600  
 Harris, 313, 319, 320, 321  
 Harris, E. E., 537, 544, 559, 569, 571  
 Harris, G. C., 383  
 Harris, L. J., 537, 544  
 Harris, M., 296, 297, 307, 308  
 Harris, R. G., 286, 293  
 Harris, R. H., 501  
 Harris, S. A., 601  
 Harris, W. D., 253  
 Harrison, 447, 448, 449, 452  
 Harrison, A. J., 269, 273  
 Harrison, J. L., 108, 124  
 Harrison, J. M., 350  
 Harrison, L. E., 549, 567  
 Harrison, V. G. W., 334  
 Harry, R. J., 110, 125  
 Harsh, 647, 651  
 Harshaw Chem. Co., 191  
 Hart, J. S., 325  
 Hart, P., 174, 191  
 Hart, P. D., 578  
 Hart, W. B., 232, 669  
 Hart, W. J., jun., 543  
 Hartley, A., 108, 124  
 Hartley, G. S., 81, 93  
 Hartman, B. F., 171, 191  
 Hartmann, F. V., 27  
 Hartmann, I., 20  
 Hartung, W. F., 587  
 Hartzell, A., 450  
 Hartzler, E., 538, 545  
 Harvel Corp., 386  
 Harvey, A., 430, 434  
 Harvill, E., 450  
 Hasche, R. L., 366  
 Haselden, G. G., 23  
 Haskell, G., 494  
 Haslam, G. S., 200, 213  
 Haslem, M. E., 114, 125  
 Hasler, A. D., 667, 669  
 Hass, H. B., 77  
 Hassall, C. H., 618  
 Hassan, W. E., jun., 632  
 Hassell, C. H., 578  
 Hastings, J. H. H., 555, 568  
 Hathaway, D. H., 74, 79  
 Hauge, S., 569  
 Hausner, H. H., 292  
 Haut, I. C., 542  
 Hautot, 649  
 Hauze, A. R., 600  
 Haveg Corp., 365  
 Havens, R., 144, 145  
 Haward, R. N., 348  
 Hawley, R. W., 8  
 Haworth, W. N., 498, 503, 519  
 Hay, R. L., 542  
 Hay, W., 111, 124  
 Hayden, C. C., 466, 469  
 Hayman, R. F., 292  
 Haynes, J. L., 465, 469  
 Haynes, J. R., 142, 146  
 Hays, H. L., 233  
 Hayward, C. R., 130, 145  
 Hayward, F. W., 632  
 Haywood, G., 331  
 Head, R. B., 194  
 Healy, S. W., 108, 124  
 Heany, J. A., 292  
 Heath, G. D., 478  
 Heath, G. F., 572  
 Hebden, D., 50  
 Hedberg, J., 115, 125  
 Hedger, F. H., 599  
 Hedlin, R., 264, 272, 293  
 Heer, J., 594, 595  
 Heertjes, P. M., 493  
 Hegedus, B., 588  
 Hegsted, D. M., 484, 487  
 Hehre, E. J., 494  
 Heidenreich, R. D., 141, 146  
 Heidl, R., 395  
 Heilbron, (Sir) I., 546, 578, 587  
 Heilmann, T., 177, 192  
 Heimbach, 641, 649, 650  
 Heindl, R. A., 185, 193  
 Heinzl, J. O., 539, 545  
 Heintze, S. G., 455  
 Heise, G. W., 163  
 Heisey, L. V., 348  
 Hekman, E. E., 493  
 Helden, R. van, 382  
 Helfenberger, H., 592  
 Heller, M. E., 531, 542  
 Heller, W., 418  
 Hellman, H. M., 350  
 Hellman, N. N., 494  
 Hellyer, J. H., 18  
 Helm, E., 558, 562, 563, 570, 571  
 Helmers, C. J., 222, 233  
 Hems, B. A., 434  
 Henbest, H. B., 580  
 Henderson, L. F., 255  
 Henderson, S. J., 194  
 Hendrick, J., 294

Hendrick, L. R., 617  
 Hendricks, H. R., 145  
 Hendricks, S. B., 168, 190  
 Hendrickson, M. J., 382  
 Henick, A. S., 253  
 Henn, 643, 650  
 Henne, A. L., 77  
 Hennings, C., 526, 541  
 Henrikson, L., 332  
 Henry, K. M., 541  
 Henry, P., 417  
 Henry, T. R., 111, 125  
 Hensen, E., 542  
 Henshaw, D. M., 55  
 Herbarth, 318, 321  
 Herberg, T. H., 517  
 Herbert, D., 568  
 Herbst, E. J., 568  
 Hercules Powder Co., 314, 369, 374,  
 375, 417  
 Hernan, J., 398  
 Herman, T. J., 383  
 Hermann, F. J., 364  
 Hermanns, J. J., 405, 417  
 Hermans, 310, 311, 320  
 Herold, P. G., 293  
 Herrill, G. S., 451  
 Herschberger, A., 365  
 Hershberg, E. B., 592  
 Herz, 649  
 Herzik, G. R., 668  
 Hess, G., 545  
 Hess, H., 272  
 Hesse, H. C., 34  
 Hestrin, S., 557, 569  
 Heuer, R. P., 293  
 Heukelekian, H., 659, 661, 664, 668,  
 669  
 Heuler, J., 9  
 Heumann, T., 146  
 Heuser, L. J., 515, 517  
 Heusser, H., 589  
 Heussner, C. E., 161  
 Hewett, P. S., 365  
 Hewitt, C. H., 668  
 Hewitt, E. J., 463, 464  
 Hewlett, 438  
 Hewlett, A. M., 517  
 Hewlett, P. S., 478  
 Hey, D. H., 80, 93  
 Heymann, E., 358, 365  
 Heymans, C., 555, 568  
 Heywood, H., 24, 289  
 Hibbard, W. R., jun., 139, 146  
 Hibberd, A. D., 330, 473  
 Hibbert, D., 510, 517  
 Hibbs, A. N., 23  
 Hickey, J. S., 16  
 Hickman, J. W., 147  
 Hickman, K. C. D., 254  
 Hickson, E., 451  
 Hickson, S. A. D., 342  
 Hickson, W., 560, 570

Hiester, N. K., 328  
 Higgins, 446, 452, 633  
 Higgins, A. K., 108, 124  
 Highberger, J. H., 424, 427, 433, 434  
 Highnett, T. T., 185, 193  
 Hilbert, G. E., 498, 549, 567  
 Hilborn, M. T., 478  
 Hilditch, T. P., 254, 377, 381, 382  
 Hill, 525  
 Hill, C. V., 229, 234  
 Hill, H., 474  
 Hill, H. R., 7  
 Hill, W. L., 168, 190, 483  
 Hiller, A., 561, 570  
 Hilliard, A., 293  
 Hills, C. H., 531, 542  
 Hills, G. L., 541  
 Hills, G. M., 578  
 Hilton, R. J., 471  
 Himus, G. W., 232  
 Hind, H. L., 571  
 Hinkle, M. E., 662, 669  
 Hinman, W. F., 540, 543  
 Hinshaw, W. R., 491  
 Hinshelwood, C. N., 348  
 Hinton, V. C. L., 537, 544  
 Hippel, A. von, 193  
 Hirschhorn, H. N., 648  
 Hirschler, A. E., 13  
 Hirschmann, D. J., 527, 542  
 Hirst, E. L., 498, 517  
 Hirst, F., 534, 543  
 Hiscox, D. J., 254  
 Hitchcock, A. E., 472  
 Hoather, R. C., 654, 667  
 Hobby, G. L., 617  
 Hochberg, S., 451  
 Hochmann, J., 112, 125  
 Hodge, E. S., 457, 469  
 Hodge, J. E., 498, 549, 567  
 Hodges, K., 451  
 Hodgkiss, W. S., 456  
 Hodgson, H. H., 74, 79, 80, 81, 93  
 Hodgson, N., 567  
 Högberg, B., 564, 571  
 Hoffhine, C. E., 575, 599  
 Hoffman, 307  
 Hoffman, M. B., 471, 472  
 Hoffman-La Roche, Inc., 74, 617  
 Hoffmann, R. M., 308  
 Hoffmann, V., 292  
 Hoffpauir, C. L., 253  
 Hofmann, K., 568  
 Hofrichter, C. H., 350  
 Hofstee, J., 500  
 Hogberg, C. G., 106, 124  
 Hogg, J. A., 592  
 Hoh, S., 162  
 Hohenstein, W. P., 341  
 Hohf, J. P., 334  
 Hohn, L., 508, 517  
 Holbrook, F. L., 418  
 Holdeman, Q. L., 518

Holden, A. F., 174, 191  
 Holden & Sons Ltd., A., 386  
 Holderby, J. M., 559, 569  
 Holkesvig, O. A., 517  
 Holland, A. J., 266, 272  
 Hollett, A., 543  
 Holley, R. W., 599, 617, 632  
 Hollomon, J. H., 142, 146  
 Holly, K., 468, 469  
 Holman, R. T., 526, 541  
 Holmberg, J., 254  
 Holme, C., 229  
 Holmes, E. L., 365  
 Holmes, H. P., 145, 186, 193  
 Holmes, J. A., 656, 668  
 Holmes, J. B., 361  
 Holmes, L. E., 365  
 Holmes, W. R., 194  
 Holmgren, B., 335  
 Holroyd, R., 165, 190  
 Holst, E. C., 618  
 Holt, E. K., 253  
 Holt, M. L., 162  
 Holzworth, M. L., 146  
 Homans, L. N. S., 401, 415  
 Homme, V. B., 161  
 Honeyman, J., 516, 519  
 Hontman, J. P. W., 227, 234  
 Hood, T. A., 160  
 Hook, W. A., 518  
 Hoover, 313, 320  
 Hoover, S. R., 304, 308  
 Hopff, H., 338  
 Hopkins, D. P., 464  
 Hopkins, E. S., 185, 193  
 Hopkins, J. W., 545  
 Hopkins, R. H., 498, 546, 554, 567, 568  
 Hopton, G. U., 52  
 Horio, 312, 320  
 Hornby, F. P., 653, 667  
 Horsley, J., 331  
 Horton-Smith, C., 491  
 Hosberg, H. M., 527, 541  
 Hosman, P. D., 165, 190  
 Hotchkiss, R. D., 555, 568  
 Hothersall, A. W., 161  
 Hough, L., 517  
 Houle, 309, 320  
 House, K. R., 101  
 Houser, E. A., 364  
 Houtman, T., 343  
 Houtez, R. C., 366  
 Houwink, R., 404, 416  
 Hovers, J. N. J., 199, 213  
 Hovey, A. G., 385, 387  
 Howard, H. C., 198, 212  
 Howard, R. T., jun., 116, 125  
 Howat, D. D., 104, 105, 124, 192, 205, 214  
 Howell, S. F., 618  
 Howerton, W. W., 493  
 Howes, D. A., 221, 232, 233  
 Howes, W. A., 225, 234

Howie, T. W., 293  
 Howlett, 312, 320  
 Howlett, F. S., 470  
 Hozowsky, T., 212  
 Hrubesky, C. E., 334  
 Hu, H., 146  
 Huang, H. T., 583  
 Huang, P. Y., 130, 145  
 Huang-Minlon, 596  
 Hubbard, J. E., 498  
 Hucker, G. J., 518  
 Hudson, C. S., 516  
 Hudson, J. C., 121, 123, 126, 392, 393, 417  
 Hückel, W., 628  
 Heulin, F. E., 538, 545  
 Huff, D. E., 599  
 Hug, G. T., 308  
 Huggill, H. P. W., 366  
 Hughes, A. H., 562, 570  
 Hughes, D. L., 491  
 Hughes, E. R., 211  
 Hughes, H. S., 214  
 Hughes, J. S., 544  
 Hughes, L. E., 491  
 Hughes, M. F., 518  
 Hugill, J. T., 181, 192  
 Hulme, P. M., 112, 125  
 Hultquist, M. E., 600  
 Hultzsch, K., 353, 355, 364, 386  
 Hume-Rothery, W., 138, 146  
 Humphrey, J. C. W., 108, 109, 124  
 Hungerford Research Corp., 370  
 Hunt, 311, 320, 439, 451  
 Hunt, B. G., 161  
 Hunt, L. B., 162  
 Hunter, A. S., 454  
 Hunter, G. J. E., 541  
 Hunter, H., 546, 547, 566  
 Hunter, J. A., 596  
 Hunter, M. J., 271, 273  
 Hunter, R. B., 617  
 Hunter, R. S., 334  
 Hummer, R. W., 416  
 Hurd, D. T., 366  
 Hurst, H., 443  
 Hurst, R. R., 480  
 Hurwitz, 482, 483  
 Hurwitz, C., 455, 456  
 Hurwitz, E., 668  
 Husek, 647, 651  
 Huston, K. M., 162  
 Hutchings, B. L., 600, 601  
 Hutchins, M. C., 544  
 Hutchinson, H. E., 163  
 Hutchinson, H. M., 346  
 Hutchinson, W. S., 166, 190, 191, 542  
 Hutter, L., 293  
 Hutton, F. C., 5, 6  
 Hyams, H., 230, 234  
 Hyden, S., 486, 488  
 Hyman, M., 347  
 Hyslop, J. F., 262, 272, 293

## I

Ichisaka, V., 482, 483  
 Igolen, G., 632  
 Imhoff, C. E., 26  
 Imperial Chemical Industries, 7, 66, 67,  
 68, 69, 71, 72, 74, 76, 77, 84, 87, 90,  
 93, 98, 99, 100, 192, 366, 375, 384,  
 386, 387, 398  
 Ineson, P. J., 541  
 Ing, H. R., 597  
 Ingle, 441, 451  
 Ingols, R. S., 658, 668  
 Ingram, J. W., 450  
 Ingram, M., 521, 522, 540, 568  
 Inman, C. J., 193  
 Inouye, F., 163  
 Insley, H., 258, 271  
 Institute of Paper Chemistry, 75, 331  
 International Nickel Co., of Canada,  
 153  
 International Paper Co., 322  
 Ipatiev, V. N., 230  
 Ipsen, A. O., 145  
 Ireland, D. M., 566, 571  
 Irish, U., 541  
 Irvine, K. J., 108, 109, 124  
 Irwin, C. F., 398  
 Irwin, J. T., 292  
 Isaacs, D. J., 176, 192  
 Isbell, H. S., 518  
 Isbell, W. T., 145  
 Ischaert, L., 567  
 Iselin, E., 81, 93  
 Islip, H. T., 621, 631  
 Ittyachan, C. T., 621, 631  
 Ivarsson, B., 334  
 Iverson, J. O., 233  
 Iwamoto, 649  
 Iwasaki, I., 212

## J

Jack, J., 371  
 Jackson, 440, 451  
 Jackson, E. B., 618  
 Jackson, J., 507, 517  
 Jackson, J. M., 543  
 Jackson, J. S., 232  
 Jackson, L. R., 146  
 Jackson, M. J., 478  
 Jackson, R., 223, 233  
 Jacob, K. D., 480, 483  
 Jacob, W. A., 253  
 Jacobs, H. L., 177, 192  
 Jacobs, J. H., 161  
 Jacobs, S. E., 442  
 Jacobsen, A. E., 293  
 Jacobsen, S., 272

Jacobson, 435, 451  
 Jacobsson, B., 564, 571  
 Jacoby, A. L., 10, 27  
 Jacquet, P. A., 162  
 Jaffe, S. S., 163  
 Jaffee, R. I., 145  
 Jahn, C. A. H., 162  
 Jahnus, F. W., 544  
 Jahoda, 648, 651  
 Jakaboin, J. J., 167, 190  
 James, 633, 636, 649  
 James, E., 455  
 James, E. M., 554, 568  
 James, G. B., 32  
 James, H. C., 518  
 James, M., 173  
 Janes, M., 163  
 Jann, G. J., 618  
 Jansen, J. E., 344  
 Janssen, A., 372  
 Jansson, S., 103, 124  
 Japhe, H., 597  
 Jargotorff, G., 371  
 Jarnold, W. W., 225, 234  
 Jarvis, F. G., 604, 617  
 Jayme, 368  
 Jayme, G., 322, 324, 326, 333  
 Jayne, D. W., 365  
 Jean, 118, 126  
 Jeanes, 518  
 Jeanloz, R. W., 516, 519  
 Jebson-Marwedel, H., 260, 268, 272  
 Jeger, O., 632  
 Jelinek, V. C., 618  
 Jolley, 646, 651  
 Jellinek, B., 498, 567  
 Jenkins, M. T., 495  
 Jenkins, S. H., 659, 668  
 Jenkinson, J. R., 205, 214  
 Jenness, L. C., 327  
 Jennings, 645, 651  
 Jennings, C. W., 161  
 Jennings, S. F., 331  
 Jennings, W. H., 326  
 Jenny, 643, 649, 650  
 Jenny, F. J., 14  
 Jensen, A. B., 540  
 Jensen, J., 500  
 Jensen, K. E., 661, 669  
 Jensen, V., 479, 480  
 Jensen, N. C., 176, 192  
 Jergens, A. N., 255  
 Jernstedt, G. W., 162  
 Jesser, H., 538, 545  
 Jicwood Ltd., 365  
 Jimenez, M. A., 542  
 Joachim, W. F., 161  
 Jørgensen, A., 546  
 Jørgensen, H., 570  
 John, G. R., 146  
 John, L. M., 254  
 Johns, C. K., 569  
 Johnson, A. L., 24, 291

Johnson, E. P., 491  
 Johnson, H. G., 14  
 Johnson, H. L., 397, 398  
 Johnson, H. V., 540  
 Johnson, J. A., 292, 529, 542  
 Johnson, J. R., 270, 273  
 Johnson, M. J., 604, 617, 669  
 Johnson, P. H., 347  
 Johnson, T. L., 593  
 Johnson, W. E., 207, 214  
 Johnson, W. S., 595  
 Johnson Matthey & Co., Ltd., 292  
 Johnston, N. F., 529, 542  
 Johnstone, D. B., 617  
 Johnstone, H. F., 381  
 Johnstone, S. J., 166, 174, 190, 191  
 Johnstone-Wallace, D. B., 465, 469  
 Johnstown, F. B., 474  
 Jolly, A. H., 111, 125  
 Jones, B. E., 472  
 Jones, D. G., 398  
 Jones, E., 20  
 Jones, E. E., 669  
 Jones, E. P., 416  
 Jones, F. L., 432, 434, 437  
 Jones, F. W., 115, 125  
 Jones, G. F., 7  
 Jones, G. O., 262, 263, 272  
 Jones, G. W., 166, 190  
 Jones, H., 343, 373, 394, 395  
 Jones, H. A., 444  
 Jones, J. K. N., 498, 508, 509, 517, 562,  
     570  
 Jones, J. R. E., 667, 669  
 Jones, J. T., 264, 272  
 Jones, L. M., 491  
 Jones, M. E., 417  
 Jones, M. J., 580  
 Jones, N. W., 473  
 Jones, P. F., 617  
 Jones, R. G., 68, 77, 599, 618  
 Jones, S., 56  
 Jones, T. S. G., 576, 600, 618  
 Jones, T. T., 352, 364  
 Jones, W. H., 225, 234  
 Jones, W. J., 225, 234  
 Jones, W. M., 421, 433  
 Jonsen, B. W., 145  
 Jordan, L. A., 381  
 Jordan, P. E., 200, 213  
 Joseph, H. G., 571  
 Joshi, M. L., 632  
 Joshua, J. O., 491  
 Joslin, C., 371  
 Joslyn, D. A., 572, 577  
 Joyce, D., 41, 106, 124  
 Joyce, R. M., 362, 366  
 Juillerat, A., 569  
 Jukes, T. H., 580  
 Julian, P. L., 584, 589  
 Jungherr, E., 491  
 Junowicz-Kocholaty, R., 618  
 Jurisch, 311, 320

## K

Kachmar, J. F., 668  
 Kaczka, E. A., 601  
 Käpernick, E., 160  
 Kaoss, G., 527, 541  
 Kagawa, I., 369  
 Kahler, D., 654, 667  
 Kahn, S., 579  
 Kalinske, A. A., 666, 669  
 Kalkar, G. M., 254  
 Kaloyereas, S. A., 543  
 Kamecki, J., 497  
 Kameth, M. R., 631  
 Kamin, C. G., 350  
 Kanagy, J. R., 429, 430, 434  
 Kanamura, K., 372  
 Kandiner, H. J., 28, 184, 193  
 Kane, G. P., 178, 192  
 Kaplan, D., 544  
 Kaplan, N., 30  
 Kaplovsky, A. J., 661, 668  
 Kapoor, O. S., 254  
 Kappelmeier, C. P. A., 379, 382  
 Karassik, I., 7  
 Karas, A., 389  
 Karimullah, 254  
 Karlson, A. G., 491  
 Karman, G., 254  
 Karnovsky, M. L., 254  
 Karon, M. L., 253  
 Karpel, W. J., 584  
 Karrer, P., 579, 581, 585, 600  
 Karthauser, F. B., 214  
 Kastner, H., 132, 145  
 Kathalia, Y., 254  
 Kathriner, A., 583  
 Katz, A., 591  
 Katz, D. L., 6, 10, 231  
 Katz, S., 213  
 Katznelson, H., 565, 571  
 Kauer, K. C., 73  
 Kauffmann, A. R., 133, 145  
 Kaufman, C. W., 545  
 Kautz, K., 292  
 Kayan, C. F., 8  
 Kearns, H. G. H., 476, 478  
 Keaton, J., 330  
 Keefer, C. E., 660, 668  
 Keenan, H. W., 393  
 Keil, H. R., 128, 145  
 Keleman, D. K., 161  
 Keller, 644, 650  
 Keller, E. L., 328  
 Keller, W. D., 293  
 Kelley, C. E., 491  
 Kelley, O. J., 454  
 Kellogg, E., 162  
 Kelly, 649  
 Kelly, A., 283  
 Kelly, H. E., 560, 563, 570, 571  
 Kelly, L. E., 333  
 Kemp, L. C., 12

- Kendall, 639, 641, 644, 650, 651  
 Kendall, J. D., 83  
 Kendall, J. T., 186, 193  
 Kennedy, A. B., 12  
 Kennedy, D. R., 668  
 Kennedy, H. L., 291  
 Kennedy, J. S., 128, 144, 440, 478  
 Kenney, E. F., 561, 570  
 Kenten, R. H., 430, 434  
 Kenworthy, A. L., 472  
 Kenyon, R. L., 12, 381  
 Keresztesy, J. C., 601  
 Kerley, R. V., 234  
 Kerlogue, R. H., 24  
 Kermack, W. O., 555, 568  
 Kern, 350  
 Kerr, C., 214  
 Kerr, H., 43  
 Kerr, J. S., 209, 215  
 Kerr, R. W., 495, 549, 567  
 Kerschbaum, 596  
 Kertesz, Z. I., 542  
 Kesler, C. C., 500  
 Kesterton, A. J., 111, 125  
 Ketchum, B. H., 391, 393  
 Keuning, 648, 651  
 Key, T. D., 653, 667  
 Keyes, 641, 650  
 Keyworth, W. G., 567  
 Khasilev, V. I., 206, 214  
 Khastagir, H., 632  
 Khayatt, R. M., 307, 308  
 Khrisanfova, A. I., 212  
 Kibler, 645, 651  
 Kidd, D. A., 587  
 Kiefer, C., 292  
 Kiel, J. W., 524, 541  
 Kiemeier, F., 468, 470  
 Kiesel, G. K., 491  
 Kikuchi, 649  
 Kilbourne, F. L., 418  
 Kilner, W., 27  
 Kincaid, R. R., 480  
 King, A., 145  
 King, C. G., 553, 568  
 King, F. E., 587  
 King, H., 584  
 King, J. A., 586  
 King, J. G., 64, 196, 211  
 King, N., 541  
 King, P., 393, 417  
 King, R., 162  
 King, R. O., 225, 234  
 King, W., 161  
 Kingkade, M. J., 617  
 Kingsbury, R. M., 329  
 Kinney, C. R., 199, 212  
 Kintz, G. M., 166, 190  
 Kipps, E. H., 457, 469  
 Kirby, K. S., 425, 433  
 Kirkby, H. W., 116, 125  
 Kirn, W., 349  
 Kirov, N. Y., 203, 213  
 Kirschbaum, E., 15  
 Kirschbaum, K., 231  
 Kite, R. P., 7  
 Kittel, H., 358, 368  
 Kittrell, F. W., 652, 667, 669  
 Klaarenbeek, F. W., 268, 272  
 Klassen, C. W., 663, 669  
 Klee, L., 501  
 Kleedorfer, 596  
 Kleiderer, 599  
 Kleikamp, J. H. B., 526, 541  
 Klein, H., 657, 668  
 Klein, S., 621, 631  
 Kleinzeller, A., 526, 541  
 Kleptko, E., 212  
 Klima, J., 213  
 Klimet, J. W., 569  
 Kline, G. M., 366  
 Kline, H., 365  
 Klingsberg, A., 575  
 Klosa, J., 626, 631, 632  
 Kluyver, A. J., 560, 570  
 Klyachko, Y. A., 119, 126  
 Knapp, F. J., 416  
 Knauber, H., 550, 567  
 Kneen, E., 551, 568  
 Knewstubb, N. W., 365  
 Knibbs, N. V. S., 180, 192  
 Kniel, J., 217, 232  
 Knight, G. S., 61  
 Knight, H., 478  
 Knight, H. A., 160, 292  
 Knight, H. B., 385, 387  
 Knott, 641, 642, 650  
 Knox, E. M., 212  
 Kobayashi, 312, 320  
 Kobe, K. A., 165, 190  
 Kohlitsky, 437  
 Koch, J. R., 253  
 Koch, T., 374  
 Koch, W., 544  
 Kochler, J. S., 23  
 Koehntitzky, O. W., 667, 669  
 Kocer, M., 583  
 Kodak, Ltd., 100  
 Kodicek, E., 544  
 Köhle, H., 345  
 Koehler, W. A., 662, 669  
 Kohman, E. F., 631  
 Koifman, B. E., 212  
 Kokes, E. L., 304, 308  
 Kolachov, P., 565, 566, 571  
 Kolb, F. J., 364  
 Kolb, O. K., 193  
 Kolthoff, 449  
 Kominek, E. G., 25, 655, 668  
 Kon, S. K., 541  
 Kondo, 312, 320  
 Konen, J. C., 382  
 Koniuszy, F. R., 601  
 Konkle, G. M., 417  
 Konzo, S., 215  
 Koonz, C. H., 540

Kooy, 637, 649  
 Kopaczewski, I. W., 416  
 Kopecki, E. S., 113, 125  
 Koppers Co., 201, 369  
 Kopplin, F. W., 516  
 Koritskii, V. G., 118, 125  
 Korman, J., 596  
 Korn, A. H., 308, 313, 320  
 Kornfeld, E. C., 618  
 Korolov, I. L., 213  
 Korshak, V. V., 361, 366  
 Kosikowsky, F. V., 541  
 Kott, A., 502  
 Kouchairevitch, N. R., 201, 212  
 Kradjčinović, M., 496  
 Kraft, E. A., 213  
 Kraitzer, I., 387, 393  
 Kramer, A., 534, 543  
 Kramer, H. P., 668  
 Kramer, M. L., 602  
 Kramers, W. J., 200, 213  
 Kratky, O., 420, 433  
 Kratz, A. P., 215  
 Krause, B., 546  
 Krause, D. E., 213  
 Kraybill, H. R., 544  
 Krebs, H. A., 491  
 Kreidl, N. J., 256, 269, 271, 273  
 Kremen, S. S., 424, 433  
 Kressman, T. R. E., 365  
 Krider, J. L., 468, 470, 484, 487, 545  
 Krieble, R. H., 364  
 Krishna, S., 631  
 Krishnaswamy, K. G., 549, 567  
 Krist, 297, 307  
 Kritzinger, C. C., 423, 427, 433, 434  
 Kröger, F. A., 189, 194  
 Kroll, A. E., 21  
 Kroll, W. J., 131, 145, 186, 193  
 Kropa, E. L., 386  
 Krugelis, E. J., 557, 569  
 Kruse, N. F., 12  
 Krynitsky, J. A., 77  
 Kubaschewski, O., 129, 145  
 Kucera, E., 213  
 Kudriavtzev, V. I., 550, 567  
 Kudva, K. G., 631  
 Kudva, K. T., 631  
 Kuehl, F. A., 575, 599, 618  
 Küntzel, A., 425, 434, 541  
 Kuh, E., 600  
 Kuhl, H., 291  
 Kuhlmann, 98, 99, 100  
 Kuhn, B. M., 417  
 Kuhn, E. M., 212  
 Kuhn, H., 418  
 Kuhn, W., 418  
 Kukhareenko, T. A., 215  
 Kukuk, P., 212  
 Kulka, D., 548, 559, 567, 569  
 Kullgren, 312, 320  
 Kuloor, N. R., 178, 192  
 Kumar, A., 254

Kunin, R., 358, 365  
 Kunststoffe, 350  
 Kuntz, E., 538, 545  
 Kunzel, 525  
 Kura, J. G., 133, 145  
 Kurman, W., 542  
 Kushner, 593  
 Kutyanin, G. I., 426, 434  
 Kwauk, M., 7  
 Kwit, N. T., 602  
 Kyame, L., 254, 541

## L

Labatut, R., 451, 632  
 Lacey, M. S., 618  
 Larcombe, P., 137, 146, 162  
 Laer, M. van, 554, 568  
 La Face, F., 62 2, 631  
 La Follette, J. R., 451  
 Lafond, J., 536, 544  
 La Forge, 436  
 Lagally, P., 345  
 L'Air Liquide, 193  
 LaJoy, M. H., 335  
 Lake, G. F., 27  
 Lakritz, D. E., 622, 631  
 Lal, K. N., 466, 469  
 Lamattina, T. P., 395  
 Lamb, A. F., 294  
 Lamb, F. C., 543  
 Lamb, J., jun., 469  
 Lambert, A., 398  
 Lameck, P., 41  
 La Mer, V. K., 451, 478  
 Lammers, H. B., 208, 214  
 Lamoén, F. L. J., 500  
 Lampen, J. O., 580  
 Lampitt, L. H., 501  
 Landau, N., 463, 464  
 Landau, R., 666, 669  
 Landon, W. E., 451  
 Landy, M., 618  
 Lane, F. G., 229, 234, 417  
 Lane, J. C., 231  
 Lane, M., 25, 668  
 Lane, R. B., 109, 124  
 Laneau, R., 563, 571  
 Lanen, J. M. van, 565, 571  
 Lang, K., 542  
 Lange, W. H., 446, 452, 479, 480  
 Langelier, W. F., 658, 668  
 Langeman, H., 292  
 Langer, P., 491  
 Langlykke, A. F., 502, 551  
 Laporte Ltd., B., 194  
 Lapple, C. E., 6  
 Lardy, H. A., 441, 451, 568  
 Large, E. C., 467, 469  
 Larmouth, W., 502  
 Larson, A. T., 338  
 Larson, L. M., 599

- Lasman, W. C., 567  
 Lassen, R., 668  
 Latchum, J. W., 172, 191  
 Latham, G. H., 350  
 Lathrop, E. C., 518  
 Lathrop, F. H., 478  
 Latin, A., 137, 146  
 Latta, R., 439, 451  
 Laufer, S., 560, 570  
 Laundry, E. A., 49  
 Laurent, P., 136, 146, 254  
 Laurin, F., 292  
 Lauterbach, K. E., 340  
 Lavers, C. G., 542  
 Lawlor, F. E., 395  
 Lawrence, 321  
 Lawrie, W. B., 20  
 Laws, E. Q., 192  
 Laws, S. G., 491  
 Lawton, F. W., 202, 213  
 Lazzari, G., 166, 190  
 Lea, C. H., 541  
 Lea, F. M., 293  
 Leach, B. E., 578  
 Leaf, W. B., 656, 668  
 Lear, B., 479, 480  
 Leavenworth, C. S., 561, 570  
 Le Baron, R., 73  
 Le Beau, D. S., 413, 418  
 Le Bras, J., 404, 416  
 Leckie, A. H., 110, 124  
 Lecuir, R., 278  
 Ledingham, G. A., 565, 571  
 Ledwith, R. J., 394, 395  
 Lee, E., 386  
 Lee, E. S., 28  
 Lee, F. A., 532, 542, 543  
 Lee, H., 113, 125  
 Lee, J. A., 190, 233, 329  
 Lee, J. Y., 359, 365  
 Lee, P. J. van der, 539, 545  
 Lee, R. J., 396, 397  
 Lee, S. W., 600  
 Leeper, G. W., 457  
 Leermakers, 642, 650  
 Lees, D. C. G., 134, 145  
 Lees, G. M., 38, 211, 229  
 Lees, H., 455, 456, 483  
 Lees, K. H., 545  
 Leffert, C. B., 222, 233  
 Legge, N. R., 418  
 Leghorn, P. M., 618  
 Le Grip, R. G., 290  
 Lehman, E., 494  
 Lehn, G. J., 555, 569  
 Leicester, Lovell & Co., Ltd., 365  
 Leichsenning, J. M., 472  
 Leiserson, L., 73  
 Leistner, 644, 650  
 Lejeune, G., 173, 191  
 Lembcke, R. E., 365  
 LeMense, E. H., 571  
 Lemm, 316, 317, 321  
 Lemoigne, M., 559, 570  
 Lemon, H. W., 254  
 Lemoyne, 518  
 Lendal, F., 330  
 Lenhart, W. B., 177, 192  
 Leon, A. P., 600  
 Leohard, N. J., 584  
 Leonard, R. H., 669  
 Lepetit, F., 401, 416  
 Lepper, W., 533, 543  
 Leppla, P. W., 173, 191  
 Lerberghe, K. van, 383  
 Lerman, F., 12  
 Leschen, J. G., 142, 146  
 Leszynski, 639, 650  
 Letort, Y., 179, 192, 289  
 Leva, M., 6, 8  
 Levecque, M., 292  
 Levenson, G. I. P., 641, 644, 650  
 Levenson, H. S., 254  
 Lever Bros. & Unilever Ltd., 255, 381  
 Leverenz, H. W., 194  
 Levesque, C. L., 358, 365  
 Levi, A. A., 607, 617  
 Levi, L. I., 214  
 Le Vine, R. Y., 663, 669  
 Levine, W. D., 162  
 Levy, C. B., 618  
 Levy, J., 191, 366  
 Lewis, C. R., 162  
 Lewis, E. B., 481, 483  
 Lewis, E. S., 329  
 Lewis, H. C., 24, 447, 449, 451, 452, 461  
 Lewis, H. F., 327, 664, 669  
 Lewis, J. C., 618  
 Lewis, N. F., 491  
 Lewis, V. M., 473  
 Lewis, W. K., 202, 213  
 Lewthwaite, R., 600  
 Ley, H. L., 600, 618  
 Leyton, E. McP., 364  
 Libbey-Owens-Ford-Glass Co., 365  
 Liberzon, E. A., 213  
 Licht, W., 14  
 Lichtstein, H. C., 568  
 Liebich, H., 525, 541  
 Lietzke, M. H., 162  
 Lightbody, H. D., 527, 542  
 Lilley, H. S., 352, 364, 380, 382, 383, 386  
 Lillie, H. R., 262  
 Lilly & Co., E., 70, 617  
 Lilly Laboratories for Clinical Research, 573  
 Lincoln, C., 466, 469  
 Lincoln, J., 72  
 Lindberg, I., 296, 308  
 Lindberg, J., 423, 433  
 Lindberg, N. J., 332  
 Linde Air Products Co., 192  
 Lindley, H., 299, 308  
 Lindsley, C. H., 405, 416, 500

Line, E. C., 432, 434  
 Linsley, E. G., 469  
 Lintner, C. J., 75  
 Lipmann, F., 568  
 Lippman, A., jun., 172, 191  
 Lips, H. J., 254, 541  
 Lipson, M., 307, 313, 320  
 Lisk, G. F., 77  
 Little, A. T., 146  
 Little, G. E., 365  
 Little, K., 146  
 Little, Inc., A. D., 365  
 Littlejohn, W. R., 627, 628, 629, 632  
 Littleton, J. T., 262  
 Livermore, A. H., 599  
 Lloyd, R., 161  
 Lloyd, R. R., 161  
 Locker, J. R., 6  
 Lockers, Ltd., 6  
 Lockwood, A. R., 518  
 Lodder, J., 557, 569  
 Löf, G. O. G., 8  
 Löf, O. G., 214  
 Loewe, L., 617  
 Lofgreen, C. P., 469  
 Logan, R. K., 549, 567, 570  
 Logan, R. P., 664, 669  
 Loginova, 460, 464  
 Lollar, R. M., 424, 433  
 Long, K. E., 174, 191  
 Long, P. H., 577  
 Long, R., 292  
 Long, R. S., 86  
 Longenecker, H. E., 539, 545  
 Longenecker, L., 110, 125  
 Longhof, A., 294  
 Lormand, C., 537, 544  
 Lorne, H. T., 229, 234  
 Loshin, J., 12  
 Loucks, C. A., 517  
 Loughheed, E. H., 326  
 Loughlin, J., 211  
 Loury, M., 253  
 Love, K. S., 359, 368, 460, 464, 481, 483  
 Love, T., 366  
 Loveless, A. H., 167, 190  
 Lovell, W. F., 234  
 Low, 521  
 Lowdermilk, F. R., 193, 364  
 Lowe, A., 398  
 Lowe, B., 540  
 Lubahn, J. D., 142, 146  
 Lubatti, 444, 445, 446, 447, 448, 449, 450, 451, 452  
 Lucas, R. E., 473  
 Luce, W. A., 29  
 Lukasiewicz, 234  
 Luckwill, L. C., 471  
 Lui, E., 517  
 Lukens, H. C., 161  
 Lukens Steel Co., 157  
 Lumb, C., 661, 668

Lumb, M., 617  
 Lumie, R. K., 171, 191  
 Lund, A., 382, 565, 571  
 Lund, G., 8  
 Lundén, R., 567  
 Lundgren, 649  
 Lundh, 649  
 Lundin, H., 551, 568  
 Lunn, H. B., 163  
 Lutz, J. F., 482, 483  
 Luvisi, F. P., 434  
 Lyandres, A. Z., 163  
 Lyle, A. K., 260, 272  
 Lyle, O., 46, 195, 211  
 Lyman, C. M., 253  
 Lyman, T. R., 289  
 Lyons, E. J., 21  
 Lyons, J., 524, 541  
 Lyons, S. C., 24  
 Lyra, 320, 321

## M

Macadam, A. C. F., 292  
 McAdams, W. H., 10  
 McAllister, M. H., 193  
 McBain, J. W., 254, 255  
 McBee, E. T., 77  
 Macbeth, A. K., 630, 632  
 McBeth, C. W., 479, 480  
 McCance, A., 293  
 McCarthy, J. L., 165, 190, 327, 328, 426, 434, 467, 469, 669  
 McCaslin, L. M., 28  
 McCaslin, L. S., 232  
 McCay, C. M., 543  
 Machlis, S., 255  
 McCleary, C. D., 416  
 McClure, H. B., 217, 232  
 McCollam, M. E., 463, 464  
 McCollum, O. H., 417  
 McCole, E. M., 400, 415, 416  
 McConnell, D., 292  
 McConnell, R. J., 302, 308  
 Maceormac, M., 63  
 McCormick, R. H., 233  
 McCowen, J. L., 562, 570  
 McCready, R. M., 536, 544  
 McCubbin, W. A., 479, 480  
 McCulloch, E. C., 569  
 McDaniel, L. E., 616  
 McDonald, F. J., 478  
 Macdonald, H. A., 469  
 McDonald, H. J., 114, 122, 125, 126  
 MacDonald, J. C., 20  
 Macdonald, N. S., 600  
 MacDougall, D., 535, 544  
 McDowell, S. J., 292  
 Macek, T. J., 491  
 McElroy, L. A., 542  
 McElroy, O. E., 553, 568  
 Macey, H. H., 275, 276, 291

- Macfarlan, J., 467, 469  
 McFarlane, A. F., 22  
 McFarlane, V. H., 527, 542  
 McGavack, J., 416  
 Macgill, C. D., 7  
 McGinty, L., 344  
 McGlashan, J., 519  
 McGovern, J. J., 384, 386  
 McGovern, J. N., 328  
 McGovran, E. R., 436, 450  
 McGregor, M. A., 533, 543  
 McGregor, W. G., 467, 469  
 Macguffe, J., 390  
 McHard, J. A., 366  
 McHargue, J. S., 456, 457, 469, 482, 483  
 McIlroy, R. J., 516, 519  
 McIntosh, D. C., 324  
 MacIntyre, W. H., 192  
 McIsaac, F. M., 467, 469  
 Mack, D. E., 21  
 McKeag, A. H., 189, 190, 194  
 McKee, J. H., 200, 213, 298  
 McKee, R. C., 334  
 McKennon, F. L., 416  
 Mackenzie, C. A., 366  
 Mackenzie, E. F. W., 653, 667  
 McKenzie, H. M., 322  
 Mackenzie, J., 106, 124, 293  
 McKenzie, J. P., 417  
 McKeown, M. R., 196, 211  
 McKern, H. H. G., 631  
 McKinney, S. E., 491  
 McKinnis, A. C., 15  
 McKnight, F., 162  
 Mackowsky, M. T., 197, 212  
 MacLachlan, J. D., 457, 467, 469  
 McLaren, A. D., 319, 321, 350  
 MacLaurin, D. J., 325  
 MacLay, M. H., 491  
 MacLay, W. D., 544  
 McLean, I. W., 572  
 McLean, W., 577  
 McLeish, N., 350  
 McLendon, V. J., 184, 193  
 McLeod, D. H., 491  
 McLeod, J. M., 103, 124  
 Macmahon, J. D., 191  
 MacMasters, M. M., 498  
 McMillan, T. J., 543  
 McMillen, W. N., 486, 488  
 McMullen, J. C., 262, 272  
 MacMullin, R. B., 73, 171, 172, 191  
 McMurtrie, D. H., 368  
 Macnair, P. M., 113, 125  
 McNally, P. A., 601  
 McNeeley, W. H., 517  
 McNeil, E., 491  
 McNeill, H. L., 127, 144  
 McNulty, J. S., 482, 483  
 McNutt, W. S., 568  
 McQueen, 649  
 MacSwain, J. W., 469  
 McTaggart, F. K., 174, 191, 387, 393  
 McVey, J. F., 168, 190  
 McVickar, M. H., 457  
 McWhirter, M., 599  
 Maddison, L., 254  
 Mader, W. J., 617  
 Madge, E. W., 401, 416  
 Madigan, D. G., 618  
 Madigan, J. C., 416  
 Madoraky, S. L., 349  
 Madow, B., 416  
 Maetzig, 644, 650  
 Mager, J., 569  
 Magnani, A., 584  
 Magnesium Elektron Ltd., 193  
 Magnesium Metal Corp. Ltd., 192  
 Magot-Cuvru, F., 54, 198, 212  
 Maguire, J. J., 25  
 Mahant, S. D., 254  
 Mahchenko, A. L., 563, 571  
 Mahla, E. M., 122, 126  
 Maier, F. J., 657, 668  
 Majumbar, S. K., 268, 272  
 Majumdar, J. N., 213  
 Makower, B., 527, 542  
 Malkan, S. A., 469  
 Malkar, 466  
 Maller, R. K., 79  
 Mallinckrodt Chemical Works, 70  
 Mallmann, W. L., 654, 667  
 Mallon, A. R., 292  
 Malin, 369  
 Maltezeva, 647, 651  
 Mangun, G. H., 450  
 Manly, W. D., 136, 146  
 Mann, C., 418  
 Mann, J., 417  
 Mann, M. J., 599  
 Mann, P. J. G., 455  
 Manning, G. K., 146  
 Mantell, C. L., 161  
 Mantius, E., 169, 191  
 Manyam, K. B., 659, 668  
 Mapson, L. W., 537, 544  
 Mapstone, G. E., 226, 234  
 Marathon Corporation, 327  
 Marbaker, E., 292  
 Marcali, K., 434  
 Marconi Wireless & Telegraph Co., 188, 194  
 Marggraff, I., 538, 545  
 Margolit, J., 570  
 Mariani, E., 517  
 Marier, J. R., 542  
 Marine Magnesium Products Corp., 192  
 Mark, H., 372  
 Mark, H. F., 295, 308, 309, 310, 314, 319, 320, 321  
 Mark, I., 161  
 Markham, A. E., 165, 190, 327  
 Markowitz, M., 393  
 Marks, H. C., 554, 568  
 Marles, D., 117, 126

- Maron, S. H., 416  
 Marquardt, R. R., 544, 571  
 Marriner, D. E., 327  
 Marsden, L., 19  
 Marsden, P. S. S. F., 571  
 Marsh, A. W., 457  
 Marsh, D. F., 585  
 Marshall, D. L., 122, 126  
 Marshall, E. K., 618  
 Marshall, F. T., 300, 307, 317, 321  
 Marshall, J., 478  
 Marshall, J. B., 541  
 Marth, P. C., 464, 470  
 Martin, 311, 312, 320  
 Martin, C. F., 82, 94  
 Martin, C. J., 254, 526, 541  
 Martin, D. D., 588  
 Martin, G., 381, 404, 416  
 Martin, G. T. O., 292  
 Martin, H., 443, 478  
 Martin, J. P., 512, 518  
 Martin, J. T., 435  
 Martin, S., jun., 543  
 Martin, S. M., 161  
 Martin, S. R. W., 383, 386  
 Martynoff, M., 81, 82, 93, 94  
 Marvel, C. S., 349, 384, 386, 417  
 Mashovets, V. P., 163  
 Mason, A. C., 446, 452  
 Mason, J. B., 209, 215  
 Mason, R. B., 160  
 Mason, S. G., 334  
 Massart, L., 556, 569  
 Massee, A. M., 567  
 Massey, L. M., 479, 480  
 Mast, W. C., 417  
 Mather, 635, 649  
 Mathers, F. C., 161  
 Matheson, D., 19  
 Mathieson Alkali Works, 73, 77, 174, 191  
 Mathieson Chemical Corp., 616  
 Mathur, K. G., 193  
 Matsuoko, 649  
 Mathew, G. E. A., 437  
 Mathew, P. K., 253  
 Matthaes, K., 114, 125, 346  
 Matthews, E. M., 469  
 Mattil, K. F., 253, 254  
 Mattis, P. A., 491  
 Mattson, F. H., 544  
 Mattson, S., 533, 543  
 Mattyasvosky-Zsolnay, L., 282, 292  
 Matuszak, M. P., 171, 191  
 Maude, A. H., 172, 191  
 Mauss, H., 598  
 Maxwell, A. A. F., 66  
 Maxwell, B. L., 255  
 Maxwell, C. S., 332  
 May, T. P., 160  
 May & Baker, 547  
 Maycock, W. d'A., 518  
 Maver, F. W., 200, 213  
 Mayer, M., 193  
 Mayers, W. M., 469  
 Mayhall, M., 568  
 Mayne, J. E. O., 123, 126, 393  
 Mayor, J., 477, 478  
 Mazumdar, 312, 320  
 Mazzone, M., 162  
 Mead, T. H., 604, 617  
 Meakins, R. J., 292  
 Meara, M. L., 254, 521  
 Mecham, D. K., 529, 542  
 Mechek, V., 212  
 Mechliniski, C., 540  
 Medcof, J. C., 541  
 Medler, J. T., 469  
 Meeds, J., 118, 126  
 Meer, S. van der, 355, 364  
 Megson, N. J. L., 354, 363, 364, 366  
 Mehl, J. W., 544  
 Mehl, R. E., 116, 125  
 Mehring, A. L., 460, 464  
 Meidinger, 640, 650  
 Meisel, S. L., 81, 94  
 Meissner, H. P., 14  
 Meister, G., 162  
 Mellanby, E., 485, 487  
 Mellier, M. T., 253  
 Mellon, E. F., 313, 320, 420, 433  
 Melpolder, F. W., 224, 233  
 Melville, H. M., 232  
 Melville, H. W., 349, 351  
 Melvin, E. H., 494  
 Melzer, E., 425, 434  
 Menkart, 313, 320  
 Menon, A. K., 621, 631  
 Mera, P. J., 540  
 Mercer, A. R., 229, 234  
 Mercier, E., 213  
 Merak & Co., Inc., 76, 576, 582, 616, 617  
 Meredith, R., 306, 308  
 Merrill, H. B., 424, 433  
 Merrill, R. C., 652, 667  
 Mesrobian, R. B., 386  
 Metal Hydrides Inc., 180, 192, 193  
 Metcalf, R. L., 442  
 Meter, C. T. van, 596  
 Meunier, 321  
 Meyer, A., 203, 212, 213  
 Meyer, B. H., 538, 540  
 Meyer, F. W., 584, 589  
 Meyer, K. H., 501  
 Meyer, L. W. A., 374, 395  
 Meyerhof, O., 552, 568  
 Meyet, E., 545  
 Meystre, Ch., 589  
 Mhaskar, V. V., 254  
 Micaelli, O., 253  
 Michael, R. V., 541  
 Michaels, E. B., 255  
 Mickelson, M. N., 537, 545  
 Micucci, D. D., 348  
 Middleton, A. C., 46

- Miedel, H., 415  
 Miers, J. C., 518  
 Miescher, K., 589, 592, 593, 594, 595, 602  
 Migaki, H., 569  
 Miklowitz, J., 303, 308  
 Milas, N. A., 579, 600  
 Miles, G., 656, 668  
 Military Chemical Works, Inc., 190  
 Miller, B. S., 529, 542  
 Miller, E. E., 434  
 Miller, G. L., 434  
 Miller, H. C., 599  
 Miller, J., 599  
 Miller, K. W., 11  
 Miller, L. B., 332, 644, 650, 653, 667  
 Miller, L. H., 533, 543  
 Miller, P., 166, 167, 183, 190  
 Milliand, 307  
 Milliard, F., 303, 308  
 Millikan, C. R., 468, 469, 473  
 Millott, J. O'N., 211  
 Mills, I. W., 225, 234  
 Minchin, S. T., 227, 234  
 Mindler, A. B., 517  
 Miner, C. S., 385, 387, 396, 397  
 Mineral Oil Products, 72  
 Ministry of Fuel & Power, 58, 195, 211  
 Minnesota Mining & Manufacturing Co., 376  
 Minsell, R. I., 465, 469  
 Mintrop, R., 116, 125  
 Misch, R. D., 122, 126  
 Mishler, D. H., 485, 487  
 Missimer, J. K., 333  
 Mitchell, B. W., 588  
 Mitchell, D. J., 524, 541  
 Mitchell, J. W., 464, 466, 469, 633, 634, 649  
 Mitchell, P. D., 555, 569  
 Mitchell, T. F., 144, 145  
 Mitchell, W., 621, 627, 631, 632  
 Mitchell, W. A., 493  
 Mitra, C., 632  
 Mitra, K. K., 556, 569  
 Mitsch, E. H., 26  
 Mittou, R. G., 431, 432, 434  
 Modell, W., 602  
 Moe, O. A., 587  
 Möglich, 644, 650  
 Moeller, W. P., 371  
 Moeschlin, S., 618  
 Mohlman, F. W., 669  
 Mohr, W., 524, 526, 541  
 Moir, H. C., 545  
 Molaison, H. L., 416  
 Moll, H., 26  
 Mollet, H. W., 566, 571  
 Molurus, F., 472  
 Monaghan, J., 111, 125  
 Moncrieff, R. W., 545, 629, 632  
 Moncrieff-Carr, W., 195, 211  
 Monnet, R., 571  
 Monro, 445, 452  
 Monsanto Chemical Co., 66, 364, 386, 387  
 Montclair Research Corp., 366  
 Montel, R., 268, 272  
 Monterumici, R., 364  
 Montgomery, E. M., 498, 549, 567  
 Montmorency, W. H., 325  
 Montross, C. F., 15  
 Mo och Domjö Akt., 374  
 Moon, H. H., 472, 483  
 Moore, A. K., 293  
 Moore, H., 260, 271, 272, 273  
 Moore, J. W., 23  
 Moore, L. R., 196, 211  
 Moore, R. L., 344  
 Moore, T., 544  
 Moore, W. A., 669  
 Moran, T., 485, 487  
 Morcom, A. R., 191  
 Moreau, L., 112, 125  
 Morehead, 320, 321  
 Morehouse, C. K., 163  
 Morgan, O. M., 571, 651  
 Moritz, H., 289  
 Morize, P., 162  
 Morley, J. I., 116, 125  
 Morral, F. R., 115, 125  
 Morrell, 645, 651  
 Morrell, S. H., 233  
 Morren, G., 292  
 Morris, 300  
 Morris, D. D., 192  
 Morris, J. C., 12, 667  
 Morris, J. S., 162  
 Morris, L. M., 472  
 Morris, R. J., 82, 94  
 Morris, S. G., 254  
 Morris, T. N., 530, 542  
 Morrison, F. R., 631  
 Morrogh, H., 117, 125  
 Morse, E. V., 491  
 Morse, L. M., 161  
 Morse, P. W., 536, 544  
 Morse, R. S., 16  
 Morse, W. J., 451  
 Morton, G., 194  
 Morton, G. F., 411, 418  
 Morton, H. E., 618  
 Morton, R. A., 544  
 Moschette, D. S., 543  
 Moser, F., 465, 469  
 Moser, H. A., 254  
 Mosley, V. M., 302, 308  
 Mott, 633, 643, 649, 650  
 Mott, B. W., 146  
 Mott, N. F., 141, 146  
 Mott, R. A., 196, 211  
 Mottern, H. H., 531, 543  
 Moulds, W., 479, 480  
 Moulton, M. S., 343  
 Moulton, R. W., 167, 190  
 Mouw, J. E., 491

Movey, G. H., 77  
 Mowat, J. H., 600, 601  
 Mower, W. W., 180, 192  
 Moxness, S. K., 364  
 Moxon, 261  
 Moyer, A. J., 604, 616  
 Moyer, J. C., 543  
 Mozingo, R., 601  
 Mrak, E. M., 544, 556, 569  
 Mrazek, F. W., 517  
 Mueller, 638, 649, 651  
 Muller, H. F., 354, 364  
 Mueller, H. H., 253  
 Müller, I., 354, 364  
 Mueller, W. J., 416  
 Müller-Rid, W., 330  
 Münzinger, O. A. F., 214  
 Muirhead, 649  
 Mujica, A. C., 5, 6  
 Mulder, D., 473  
 Mulder, H., 526, 541  
 Mullen, 648, 651  
 Muller, 649  
 Muller, F. M., 324  
 Muller, S. A., 70  
 Mullins, L., 418  
 Mulon, E. F., 308  
 Mumia, M. H., 451  
 Mumford, A. R., 26  
 Munch, R. H., 28  
 Mundy, C. W. A., 381  
 Munger, C. G., 668  
 Munzinger, F., 207, 214  
 Murer, H. K., 493  
 Murgatroyd, J. B., 267, 272  
 Murnane, D., 491  
 Murneek, A. E., 470  
 Murphy, D. S., 161  
 Murphy, E. A., 401, 416  
 Murphy, J. M., 491  
 Murray, 449, 452  
 Murray, P. E., 646, 651, 658, 668  
 Murray, W. S., 350  
 Musgrave, A. J., 429, 434  
 Musil, L., 207, 214  
 Muskat, I. E., 176, 191  
 Muskett, 468, 470  
 Mustafin, I. S., 212  
 Mycalex Corp. of America, 194  
 Myer, S., 548, 567  
 Myers, H. G., 465, 469  
 Myers, R. J., 333, 358, 365  
 Myrbäck, K., 549, 567

## N

N.V. De Bataafsche Petroleum Maatschappij, 350  
 N.V. Polak & Schwarz's Essenciefabrieken, 74  
 Nabarro, F. R. N., 141, 146  
 Nadkarni, M. D., 254

Nadziakiewicz, J., 212  
 Naffziger, T. R., 364  
 Nager, U., 600, 619  
 Nagy, D. E., 178, 192  
 Najand, A., 253  
 Nancarrow, H. A., 371  
 Napier, R. L., 213  
 Naponen, G. E., 434  
 Narayan, K., 631  
 Narcus, H., 162  
 Nash, L. K., 119, 126  
 Natarajan, C. P., 544  
 National Dairy Research Labs. Inc., 617  
 National Lead Co., 393  
 National Oil Products, 70  
 Naude, T. J., 479, 480  
 Naudet, M., 253, 381  
 Naughton, J. L., 119, 126  
 Naves, Y. R., 622, 624, 626, 627, 628, 629, 630, 631, 632  
 Naylor, C. E., 162  
 Nayudamma, Y., 434  
 Neal, E. L., 331  
 Neal, O. R., 469  
 Neal, P. A., 435  
 Neale, A., 212, 314, 315, 316, 317, 321  
 Nedelmann, 201  
 Neil, E. B., 203, 212, 213  
 Neilands, J. B., 543  
 Neish, A. C., 565, 571  
 Nel, R. G., 437  
 Nelson, 436, 437  
 Nelson, F. E., 525, 541  
 Nelson, G. H., 310, 320, 323  
 Nelson, H. A., 599  
 Nelson, H. M., 364  
 Nelson, M. S., 290  
 Nelson, R. E., 366  
 Nelson, W. D., 517  
 Nesbitt, L. L., 468, 470  
 Nesom, G. H., 466, 469  
 Neufeld, H., 133, 145  
 Neukomn, H., 536, 544  
 Neumann, 647, 651  
 Nevell, 311, 321  
 Nevin, C. S., 531, 542  
 Newbold, G. T., 578  
 Newcomer, E. J., 451  
 Newell, G. W., 485, 487  
 Newell, W. C., 108, 124  
 Newhall, A. G., 446, 479, 480  
 Newhook, F. J., 468, 470  
 Newling, W. B. S., 55, 191  
 Newman, E. S., 261, 272  
 Newton, E. B., 416  
 Newton, J. S., 214  
 Newton, R. G., 405, 412, 417, 418  
 Newton, W. L., 661, 669  
 Nicholas, D. J. D., 462, 463, 464, 474  
 Nicholas, S. D., 550, 567  
 Nicholls, L., 542  
 Nicholls, M. J., 499

Nichols, A. A., 541  
 Nichols, P. L., 519  
 Nicholson, 642, 650  
 Nickerson, R. N., 308, 310, 320  
 Nickerson, W. J., 557, 569  
 Nicolai, H. W., 175, 191  
 Niederl, J. B., 596  
 Niederl, V., 596  
 Nielsen, N. A., 122, 126  
 Nieuwenhuis, K. J., 255  
 Nigam, S. S., 631, 632  
 Nihlberg, K., 355, 364  
 Nijveld, H. A. W., 418  
 Nippes, E. F., 115, 125  
 Nissen, B. H., 560, 570  
 Nitsche, H., 545  
 Nixon, J., 660, 668  
 Noble, R. J., 415  
 Noelting, G., 501, 550, 567  
 Nogrady, G., 544  
 Noll, 312, 329  
 Nolle, A. W., 411, 418  
 Nonhebel, G., 208, 215  
 Nordbloom, G. F., 167, 190  
 Nordengren, S., 459, 464  
 Nordfelt, S., 486, 488  
 Normand, C. E., 17  
 Norman-Smith, A. C., 547, 566  
 Norris, C. A., 255, 308  
 Norris, F. A., 253  
 Norris, F. W., 553, 554, 568  
 Norrish, R. G. W., 220, 233, 348, 350  
 North, R., 24  
 Northey, E. H., 600  
 Norton, 439, 451  
 Norton, A. J., 358, 365  
 Norton, F., 219, 233  
 Norton, F. H., 293  
 Norton Co., 386  
 Nott, J., 548, 567  
 Novelli, G. D., 568  
 Nozaki, H., 596  
 Nurse, R. W., 293  
 Nutting, G. C., 421, 433, 500  
 Nyman, C. J., 175, 191  
 Nystrom, G. L., 327

## O

Oberto, S., 411, 418  
 Obey, J. H., 494  
 O'Brien, A. S., 333  
 O'Brien, H. L., 27  
 O'Brien, J. E., 214  
 O'Brien, T. D., 175, 191  
 Ocean Salts (Products) Ltd., 365  
 Ochoa, S., 568  
 O'Connor, R. T., 541  
 Ode, W. H., 201, 213  
 Odier, J., 160  
 O'Donnell, I. J., 358, 365  
 O'Donnell, W. W., 528, 542

Øhlenschlager, V., 561, 570  
 Oelsen, W., 112, 125  
 O'Farrell, M., 228, 234  
 Offermanns, H., 162  
 Ogarkov, V. S., 211  
 Ogg, W. G., 461, 464  
 O'Kane, D. E., 568  
 O'Kane, D. J., 568  
 Okhotin, M. V., 267, 272  
 Olafsson, 320  
 Olcott, H. S., 308, 529, 542  
 Old, B. S., 105, 124  
 O'Leary, M. J., 333  
 Oliver, H., 292  
 Oliver, J., 255, 569  
 Olney, R. B., 22  
 Olpin, H. C., 101  
 Olsen, W. J., 465, 551, 567  
 Olshausen, J. J., 558, 565, 569, 571  
 Olschner, P. Q., 253  
 Olson, E. R., 469  
 O'Meara, R. A. Q., 601  
 O'Meara, R. G., 128, 144  
 Ondovilla, A. G., 169, 190  
 Onusaitis, B. A., 212  
 Openshaw, 582  
 Oppenheimer, H., 418  
 O'Reilly, H. J., 530, 542  
 Orekhovich, V. N., 423, 433  
 Oriel, J. A., 229, 230, 234  
 Orning, A. A., 202, 213  
 Orsoni, B., 182  
 Osmond, D. W. J., 352, 364, 382  
 Osmun, R. H., 25  
 Oss, J. F. van, 536, 544  
 Othmer, D. F., 517  
 Otsuki, H., 348  
 Overberger, C. G., 417  
 Overfell, G. G., 231  
 Owen, W. L., 513, 517, 518, 565, 571  
 Owens, H. S., 544  
 Owens-Illinois Glass Co., 259, 272  
 Oxford, A. E., 619

## P

Packer, R. A., 491  
 Padhye, 437  
 Padmos, A. A., 264, 272  
 Page, A. B. P., 444, 445, 448, 449, 450, 451, 452  
 Pai, B. R., 79  
 Paice, E. S., 402, 416  
 Paine, T. F., 576, 618  
 Painter, E. P., 468, 470  
 Pal, 312, 320  
 Palandri, G., 411, 418  
 Palin, A. T., 654, 667  
 Palit, S. R., 255  
 Palladino, A. J., 669  
 Pallo, P. E., 655, 667  
 Palmatier, E. P., 32

- Pandit, P. N., 254  
 Panouse, M. L., 545  
 Panskin, Y. M., 220, 233  
 Paquot, C., 253  
 Pardew, M. B., 409, 418  
 Parent, J. D., 7, 213  
 Parham, M. A., 483  
 Parihar, D. B., 254, 631  
 Park, J. R., 31  
 Parker, E. R., 472, 473  
 Parker, F. D., 398  
 Parker, R. G., 294  
 Parker, R. J., 289  
 Parkin, E. A., 437, 438, 478  
 Parks, L. M., 75  
 Parmar, 321  
 Parmelee, C. W., 291  
 Parrish, P., 464  
 Parry, H., 485, 488  
 Parsegian, V. L., 271, 273  
 Partridge, E. O., 403, 416  
 Partridge, N. L., 455  
 Partridge, S. M., 517, 562, 570  
 Passmore, G. H., 267, 272  
 Pasternak, R., 418  
 Patch, E. A., 491  
 Patel, S. M., 430, 434  
 Patelaki, R. A., 617  
 Paterson, D. G. P., 162  
 Pathak, H. S., 466, 469  
 Pathak, S. P., 254  
 Paton, F. J., 400, 415  
 Paton, W. D. M., 597  
 Patterson, D. G., 386  
 Patterson, J. R., 393  
 Patterson, W. I., 254  
 Patterson, W. S., 202, 213  
 Patton, E. L., 15  
 Patton, M. B., 533, 543  
 Paynaud, E., 556, 569  
 Payne, J. H., 509, 517  
 Payne, W. G., 161  
 Peacock, A. S., 213  
 Pearce, A. G., 20  
 Pearce, J. A., 541, 542  
 Pearson, H. E., 668  
 Pearson, S., 266, 272  
 Pearson, T. F., 134, 145  
 Pease, C. S., 631  
 Peat, S., 567, 570, 498, 499, 503  
 Peavy, C. C., 171, 191  
 Peck, D. R., 450  
 Peck, R. L., 575, 599  
 Pederson, C. S., 518, 531, 532, 542, 543  
 Peech, 462  
 Peel, E. W., 575  
 Peeters, G., 556, 569  
 Pehrson, S., 331  
 Pehrson, S. O., 332  
 Peirce, F. T., 306, 308  
 Pell-Walpole, W. T., 133, 145  
 Pelletier, M. H., 585  
 Pellett, F. C., 631  
 Peltier, G. L., 537, 545, 568  
 Pelopetz, M., 212  
 Peloutier, J. M., 132, 145  
 Pence, R. O., 24  
 Penfold, A. R., 631  
 Penfold, M. C., 11  
 Peng, D. H., 544  
 Peniston, G. P., 328  
 Peniston, Q. P., 165, 190, 327, 426, 434  
 Penn, F. E., 22, 532, 543  
 Penner, M. A., 577  
 Penner, S. E., 579  
 Pennington, R. J., 554, 568  
 Pennsylvania Bituminous Coal Research, Inc., 101  
 Pennsylvania Salt Manufacturing Co., 69  
 Penny, G. F., 586  
 Pepper, E. L., 105, 124  
 Percival, E. G. V., 550, 567  
 Perdue, R., 416  
 Perkalin, V. V., 81, 93  
 Perlman, D., 617  
 Permanente Metals Corp., 193  
 Permutit Co., Ltd., 365  
 Perrins, L. E., 364  
 Perry, R. L., 484, 487  
 Perrycooste, W. B. C., 160  
 Petard, P., 632  
 Petelin, G. I., 419  
 Peters, I. I., 315, 317, 321, 351, 525, 541  
 Petersen, F. A., 292, 293  
 Peterson, 314, 321  
 Peterson, E. P., 388  
 Peterson, N., 526, 541  
 Peterson, R., 543  
 Peterson, R. F., 169, 191, 304, 308  
 Peterson, W. H., 618, 669  
 Peterson, W. R., 366  
 Petit, D., 44  
 Petitpas, T., 312, 320, 374  
 Petroe, G. A., 173, 191  
 Pett, T. G., 269, 273  
 Petty, D. H., 253  
 Petty, D. S., 228, 234  
 Pexton, S., 53  
 Pfeiffer, M., 632  
 Pfister, K., 586  
 Pfizer & Co., C., 573  
 Pfizer & Co., Inc., 617  
 Phaff, H. J., 544, 556, 569  
 Phalnikar, N. L., 254  
 Pheline, J. M., 118, 120, 126  
 Phelps, R. T., 147  
 Philbrook, W. O., 111, 125  
 Philip, B., 296, 308  
 Philip, R., 594  
 Philipp, 310, 320  
 Philips, C. B., 600  
 Phillip, A. R., 110, 124  
 Phillips, 644, 650  
 Phillips, A. G., 133, 145  
 Phillips, A. W., 536, 544

- Phillips, R., 371  
 Phillips, W. M., 161  
 Phillips Petroleum Co., 67, 191  
 Pickard, J. A., 563, 571  
 Pickering, E. T., 50  
 Pickering, G. B., 233  
 Pieniazek, S. E., 542  
 Pierre, W. H., 466, 469  
 Pierson, E., 587  
 Pierson, R. M., 416  
 Pieters, H. A. J., 199, 213  
 Pietz, E., 186, 193  
 Pigford, R. L., 9  
 Pigman, W. W., 516, 519  
 Pigott, E. C., 119, 126  
 Pijoan, M., 543  
 Pike, H. H. M., 187, 194  
 Pilcher, R. W., 534, 543  
 Pilgrim, F. J., 587  
 Pillai, S. C., 668  
 Pillsburg, A. F., 455  
 Pinck, L. A., 463, 464  
 Pinkerton, C., 483  
 Pinner, M. A., 572  
 Pinoir, 636, 649  
 Piontelli, R., 161  
 Piquett, 436  
 Piret, E. L., 14  
 Pirie, N. W., 537, 544  
 Pisarenko, A. P., 212  
 Pishawikar, D. G., 254  
 Pitcher, R. P., 302, 308  
 Pitney, A. W., 213  
 Pitrot, A. R., 387  
 Pittenger, P. S., 519  
 Pittsburgh Paint & Varnish Production Club, 381  
 Pittsburgh Plate Glass Co., 191, 192  
 Piwowarsky, 108  
 Placak, O. R., 668  
 Planje, T. J., 293  
 Plankenhorn, E., 550, 567  
 Plant, D. A., 428, 434  
 Plant, J. H. G., 55  
 Plati, J. J., 600  
 Platon, M., 105, 107, 124  
 Plattner, P. A., 578, 589, 600, 619  
 Plazin, J., 561, 570  
 Plotegher, F., 198, 212  
 Plotnikov, 643, 650  
 Pluck, J. E., 109, 124  
 Plyler, 311, 320  
 Podmore, H. L., 292  
 Polansky, T. S., 199, 212  
 Polglase, W. J., 575, 576, 618  
 Polin, I. V., 113, 125  
 Politi, J., 559, 569  
 Poll, A., 27, 214  
 Pollard, A., 446, 452, 462, 464  
 Pollard, A. E., 544  
 Polson, A., 302, 308  
 Pominski, J., 416  
 Poncelet, E. H., 266, 272  
 Pons, W. A., 253  
 Poole, J. P., 267, 272  
 Poor, E. R., 105, 124  
 Poos, 441, 451  
 Popham, W. L., 480  
 Popov, P. V., 369  
 Popp, G. E., 417  
 Porai-Koshits, A. E., 81, 93  
 Porai-Koshits, B. A., 81, 93  
 Porter, 447, 645, 651  
 Porter, L. B., 517, 518  
 Porter, R. W., 20, 170, 191  
 Potter, E. V., 140, 146, 161  
 Potter, G. M., 145  
 Potter, R. L., 568  
 Potts, H. R., 130, 145  
 Potts, S. F., 477, 478  
 Potts, T. J., 481, 483  
 Pounder, D. W., 401, 416  
 Pouradier, 636, 649  
 Pow, J., 162  
 Powell, 649  
 Powell, A. R., 48  
 Powell, E. F., 410, 418  
 Powell, H. M., 354, 364  
 Powell, M. J., 545  
 Powers, H. E., 510  
 Powers, H. E. C., 517  
 Powers, P. D., 382  
 Powers, P. O., 326  
 Powers, W. L., 457, 469, 474  
 Powers, W. R., 193  
 Pranze, G., 540  
 Prasad, M., 178, 192  
 Pratt, B., 375  
 Pratt, D. M., 417  
 Pratt, R., 617  
 Pray, H. A., 122, 126  
 Preece, A., 108, 109, 124  
 Preece, I. A., 549, 550, 551, 567, 568  
 Prolong, V., 583  
 Prendergast, A. G., 331  
 Prescott, G. W., 667, 669  
 Pressey, E. F., 545  
 Pressler, E. E., 177, 192  
 Pressley, A., 543  
 Preston, 312, 320  
 Preston, F. W., 265, 266, 272  
 Preston, R. St. J., 121, 126  
 Preston, W. C., 255  
 Price, D., 330  
 Price, D. H. A., 668  
 Price, M. D., 572  
 Price, W. J., 118, 126  
 Pridham, T. G., 577  
 Prijs, B., 588  
 Prill, E. A., 450  
 Prillinger, 596  
 Prince, A. L., 469, 480, 483  
 Prins, D. A., 516, 519  
 Printy, H. C., 589  
 Pritchett, E. G. K., 354, 364  
 Probst, A. E., 109, 124

Proctor, B. E., 536, 544  
 Proctor & Gamble, 68, 253, 381  
 Proffitt, P. M. C., 264, 272  
 Proper, R. L., 497  
 Provost, R. L., 416  
 Prusoff, W. H., 553, 568  
 Pucher, G. W., 561, 570  
 Puddefoot, L., 414, 418  
 Puddington, I. E., 254, 382  
 Puig, A. C., 212  
 Pulkki, L. H., 553, 568  
 Pulp and Paper Research Institute of  
 Canada, 325  
 Pumpfrey, W. I., 115, 125  
 Purden, A. O., 294  
 Purdy, R. W., 666, 669  
 Pure Oil Co., 191  
 Purinton, H. J., 473  
 Purves, C. B., 368  
 Purvis, S. E., 568  
 Putseiko, 640, 650  
 Putz, T. J., 214  
 Puutula, K., 553, 568  
 Puzicha, I., 146  
 Pye, D. J., 656, 668  
 Pyfinch, K. A., 126, 393

## Q

Quanquin, 460, 464  
 Quastel, J. H., 463, 464  
 Quelet, 597  
 Queneau, P. E., 161  
 Quiggle, D., 233  
 Quinn, A. W., 212  
 Quinn, F. A., 418  
 Quirk, 636, 649  
 Quisno, R. A., 569  
 Quispel, A., 482, 483  
 Quisten, F. W., 145

## R

Rabak, F., 567  
 Rabinowitz, J. C., 568  
 Rabjohn, N., 418  
 Race, E., 330  
 Rachinsky, F. Y., 545  
 Rachko, V. A., 21  
 Radio Corporation of America, 82  
 Radlove, S. B., 254, 381  
 Rafikov, S. R., 361, 366  
 Ragot, S., 253  
 Rahn, O., 569  
 Rai Choudhury, A. K., 499  
 Rainard, 320, 321  
 Rainbow, C., 554, 557, 568, 569  
 Raistrick, H., 619  
 Rake, G., 618  
 Rakshit, J. N., 632

Ralph, J. C., 624, 631  
 Ramart-Lucas, (Mme.) P., 82, 94  
 Rampton, H. C., 226, 234  
 Ramsay, G. S., 419  
 Ramsbottom, J. M., 540  
 Ramsey, L. L., 254  
 Ramuz, A., 180, 192  
 Ranby, P. W., 189, 190, 194  
 Ranch, W., 308  
 Rancourt, M., 450  
 Randall, J. B., 491  
 Randall, R. L., 418  
 Randecker, L. E., 329  
 Rank, D. R., 233  
 Rank, D. J., 224, 233  
 Ransley, C. E., 133, 145  
 Rao, A. N., 168, 190  
 Rao, P. N., 632  
 Rao, R. R., 617  
 Rao, Y. D. P., 161  
 Raper, R., 584  
 Raphael, R. A., 619  
 Rashbash, D. J., 494  
 Rasmuson, A., 192  
 Rasmussen, C. L., 542, 543  
 Rathbone, 641, 650  
 Raub, E., 146, 161  
 Rauch, 320  
 Raunch, 313  
 Rausch, E., 562, 570  
 Ravald, L. A., 53  
 Ravel, J. M., 581, 582  
 Rawson, A. E., 657, 668  
 Ray, H. S., 20  
 Raymond, 437  
 Raynor, G. V., 137, 146  
 Rayonier Incorp., 375  
 Read, F. O., 513, 518, 538, 545, 559,  
 569  
 Read, J. N., 385, 387  
 Reay, D. B., 210, 215  
 Reboul, 645, 651  
 Rebuffat, A., 291  
 Reddin, L., 491  
 Reddy, D. V. S., 545  
 Redfarn, C. A., 383, 386  
 Redfern, 369  
 Redfern, S., 550, 567  
 Redmon, B. C., 178, 192  
 Redston, G. D., 263, 272  
 Reed, H. S., 473  
 Reed, R. L., 25  
 Rees, O. W., 212  
 Rees, W. J., 285, 293  
 Rees, W. P., 114, 125  
 Reeve, L., 104, 124  
 Reeves, R. E., 368  
 Regna, P. P., 577  
 Regner, W., 176, 192  
 Rehberg, C. E., 346  
 Reich, W. S., 508, 517  
 Reich, I., 255  
 Reichel, 648, 651

- Reichert, J. S., 329  
 Reichhold, Flügger, & Boecking, 386  
 Reichold Chemicals Inc., 365  
 Reichstein, T., 590, 591  
 Reid, M., 542  
 Reid, W. G., 598  
 Reidl, A. L., 177, 192  
 Reif, G., 571  
 Reigembal, L. O., 472, 483  
 Reik, R., 193  
 Reilly, J., 82, 94  
 Reiman, W., 540  
 Reimann, I., 521  
 Rein, H., 342  
 Reinders, W., 175, 191  
 Reinhach, B. J., 365  
 Reinhard, C. E., 162  
 Reinhart, F. M., 115, 125  
 Reinhold, F., 669  
 Reinsmith, G., 412, 418  
 Reitz, L. K., 333, 334  
 Reitz, L. P., 469  
 Remfry, F. G. P., 223, 233, 234  
 Resinous Products & Chem. Co., 365  
 Resuggan, J. C. L., 537, 544, 555, 569  
 Reuning, H. T., 432, 434  
 Revels, J. M., 278  
 Revercomb, H. E., 536, 544  
 Revie, J., 105, 124  
 Rexford, P., 212  
 Reynolds, D. A., 213  
 Reynolds, D. M., 618  
 Reynolds, J. W., 366  
 Reynolds, W. B., 417  
 Reynolds, W. F., 332  
 Reynoldson, T. B., 661, 668  
 Reynst, F. H., 204, 214  
 Rhead, T. F. E., 50  
 Rhines, C. E., 416  
 Rhodehamel, H. W., 599  
 Ribaud, G., 11  
 Ribeiro, O., 537, 545  
 Ribereau-Gayon, J., 556, 569  
 Rice, 648, 651  
 Rice, E. E., 540  
 Rice, R. I., 24  
 Richards, A. R., 219, 233  
 Richards, D. O., 271, 273  
 Richards, J. H., 120, 126  
 Richards, R. B., 233, 338  
 Richards, L. A., 447, 452, 454  
 Richards Chemical Works, 71  
 Richardson, 440  
 Richardson, A. R., 516  
 Richardson, C. N., 191  
 Richie, R. J., 517  
 Richter, K., 545  
 Rickes, E. L., 601  
 Rideal, E. K., 232, 316, 321  
 Riedel, L., 534, 543  
 Rieman, W., 434  
 Riess, 645, 651  
 Riester, 641, 650  
 Rietveld, M., 210, 215  
 Riganti, A. R., 254  
 Rigby, G. W., 56  
 Rigby, H. A., 348  
 Rigden, P. J., 20  
 Rigg, J. G., 147  
 Riley, F. R., 25, 517  
 Riley, H. L., 56, 197, 212  
 Riley, J. P., 254  
 Rinaldo, P. M., 10  
 Rinse, J., 29, 356, 364, 388  
 Ripper, W. E., 478  
 Rist, C. E., 498  
 Ritchie, E. G., 209, 215  
 Ritchie, E. V., 163  
 Ritman, E. L., 324  
 Rivers, J. T., 600  
 Rivett, R. W., 618  
 Rivlin, R. S., 411, 418  
 Roach, W. A., 473  
 Road Tar Research Committee, 57  
 Robblee, A. R., 485, 487  
 Roberts, A. L., 286, 293  
 Roberts, C., 556, 569  
 Roberts, E. C., 568  
 Roberts, E. J., 7, 519  
 Roberts, H. C. W., 212  
 Roberts, J., 39  
 Roberts, J. L., 465, 469  
 Roberts, L. M., 326  
 Roberts, M., 560, 570  
 Roberts, R. H., 469  
 Roberts, S. J., 491  
 Roberts, W. O., 463, 464  
 Robertson, A., 615, 618  
 Robertson, F. L., 110, 125  
 Robertson, G. W., 19  
 Robertson, R. H. S., 212  
 Robinson, 639, 650  
 Robinson, C. A., 586  
 Robinson, F. A., 537, 544  
 Robinson, H. E., 9  
 Robinson, (Sir) R., 582, 583  
 Robinson, R. R., 466, 469  
 Robinson, R. S., 383, 386, 387  
 Robinson, S. R., 366  
 Robinson, W. B., 542, 543  
 Robitschek, F. O., 93  
 Roboz, E., 519  
 Robson, H. L., 191  
 Rocca, R. J., 105, 124  
 Rock, S. M., 233  
 Rockwood, N. C., 177, 192  
 Roddy, W. J., 431, 432, 434  
 Rodel, G. F., 385  
 Rodwell, A. W., 617  
 Roebuck, D. S. P., 402, 416  
 Roedel, G. F., 387  
 Roehl, E. J., 161  
 Röhrig, H., 160  
 Rogers, 434  
 Rogers, B. A., 186, 193  
 Rogers, D., 537, 545

Rogers, E., 110, 125  
 Rogers, H. W., 325  
 Rogers, L. L., 568  
 Rogers, S. C., 544  
 Rogers, T., 20  
 Rogers, T. H., 143, 147  
 Rohner, L. V., 359, 365, 464  
 Rollason, E. C., 117, 126  
 Rollins, M. L., 416  
 Rollinson, C. L., 191  
 Roma, F., 39  
 Rominski, R., 161  
 Rommel, T., 133, 145  
 Romwalter, A., 198, 212  
 Roney, J. N., 441, 468, 470  
 Rooney, J. H., 366  
 Root, C. H., 334  
 Rose, D., 543, 565, 571  
 Rosen, R., 666, 669  
 Rosenbaum, J. B., 161  
 Rosenberg, J. E., 292  
 Rosenbaum, J. B., 161  
 Rosenfeld, M., 114, 125  
 Rosenthal, D., 292  
 Rosi, F. D., 146  
 Ross, F. F., 214  
 Ross, J., 253  
 Ross, S. D., 28  
 Ross, W. H., 481, 483  
 Rossem, A. van, 405, 416  
 Rossini, D., 217, 232  
 Rossini, F. D., 231  
 Rosted, C. O., 561, 567, 570  
 Rostler, F. S., 409, 417  
 Rotax Ltd., 191, 366  
 Roth, H., 537, 544  
 Roth, H. P., 214  
 Roth, W., 132, 145, 146  
 Rothamel, L., 333  
 Rott, 645, 650  
 Rourk, R. C., 436  
 Rouvé, A., 632  
 Roux, D. G., 631  
 Rovesti, G., 625, 631  
 Rowe, F. D., 161  
 Rowen, 311, 319, 320, 321  
 Rowland, 314, 321  
 Rowland, E. S., 116, 126  
 Rowlands, S., 599  
 Rowley, D., 599, 617  
 Rowley, F. B., 335  
 Rowse, R. H., 206, 214  
 Roy, A. N., 233  
 Rubber Research Board, 404, 416  
 Rubbo, S. D., 555, 568  
 Rubenkoenig, H. L., 569  
 Rubin, S. H., 537, 544  
 Ruchhoft, C. C., 658, 668  
 Rudolfs, W., 658, 668, 669  
 Ruemele, T., 623, 631  
 Ruf, E. W., 565, 571  
 Ruff, D. G., 562, 570  
 Ruger, M., 617

Rugg, F. M., 393  
 Ruggli, P., 81, 93  
 Ruhemann, M., 30, 32, 182, 193  
 Runford, F., 20, 31  
 Rummel, K., 209, 215  
 Rushton, J. H., 34, 59  
 Russell, 445, 447, 449, 450, 452  
 Russell, K. E., 220, 233  
 Russell, R., 292  
 Russell, R. P., 217, 232  
 Rust, J. B., 366  
 Ruston, W. R., 197, 212  
 Ruttner, O., 585  
 Ruzicka, F. C., 383  
 Ruzicka, L., 627, 629, 632  
 Rybak, B., 617  
 Rybnikov, V. A., 285  
 Rylands, J. R., 205, 214

## S

Saal, R. N. J., 224, 233  
 Sabalitschka, T., 538, 545  
 Sabon, F., 571  
 Sachanon, A. N., 358, 365  
 Sack, U., 558, 569  
 Saeman, J. F., 544  
 Safranek, W. H., 163  
 Sage, C. E., 629  
 Sagrott, P. E., 498  
 Saibel, E., 265, 272  
 Sainclair, M., 513, 518  
 St. Johnston, J. H., 562, 564, 570, 571  
 Sair, L., 501  
 Saitzew, J., 517  
 Sakal, E., 600  
 Salac, V., 563, 567, 571  
 Salamon, 629  
 Sale, J. W., 532, 543  
 Salgues, R., 632  
 Salivar, C. J., 599, 617  
 Salle, A. J., 554, 568, 618  
 Salley, D. J., 332, 365  
 Salmon, E. S., 547, 567  
 Salsas-Serra, F., 165, 190  
 Salsat, J., 518  
 Salvesen, J. R., 327, 431, 434  
 Salvetti, A., 416  
 Salvi, C., 374  
 Salzbacher, M., 69  
 Samec, M., 496, 499  
 Samuels, M. E., 417  
 Sandegren, E., 563, 564, 571  
 Sandell, W. G., 145  
 Sandermann, W., 326  
 Sanders, M., 618  
 Sanders, M. D., 663, 669  
 Sanderson, T. F., 383  
 Sandison, R., 193  
 Sandoz, Ltd., 83, 96, 100  
 Sands, G. A., 30  
 Sandstedt, R. M., 501

- Sankey, C. A., 334  
 Sansome, F. W., 498  
 Santavy, F., 591  
 Sarett, L. H., 590  
 Sargent, R. J., 223, 233  
 Sargent, E. H. G., 366  
 Sarkar, 312, 314, 320, 321  
 Sartoris, G. B., 518  
 Saslaw, O., 193  
 Sato, Y., 573, 617  
 Sattler, L., 513, 516, 518, 519  
 Sauchelli, V., 462, 464  
 Saul, H., 662, 669  
 Saulnier, A., 138, 146  
 Saunders, D. J., 8, 25  
 Saunders, D. W., 405, 416  
 Saunders, H. L., 105, 124  
 Saunders, H. S., 292  
 Saunders, J. B., 259, 263, 271, 272  
 Saunders, K. H., 80, 93  
 Sauvenier, 635, 637, 649  
 Saville, 321  
 Savoie, C. L., 504, 516  
 Savoor, S. R., 600  
 Savostianoff, E., 496  
 Sawyer, 118, 126  
 Sawyer, C. N., 668  
 Sawyer, F. A., 209, 215  
 Sawyer, W. H., 162  
 Scafe, E. T., 398  
 Scaife, C. W., 398  
 Scalf, R. E., 551, 568  
 Scanlan, P. G., 215  
 Scarr, M. P., 513, 518  
 Scarseth, G. D., 474  
 Schaefgen, J. R., 361, 366  
 Schär, A., 541  
 Schafer, E. G., 472  
 Schafer, I. M., 483  
 Schaik, T. van, 539, 545  
 Schalm, O. W., 491  
 Schauder, R., 174, 191  
 Schaufelberger, W. F. S., 386  
 Schaum, J. H., 107, 124  
 Schechter, H., 77  
 Scheibel, E. G., 14, 15  
 Scheiber, J., 354, 364  
 Scheidy, S. F., 488, 491  
 Schenk, P., 49  
 Schepartz, A. I., 254, 541  
 Schiebers, 367  
 Schildknecht, 348  
 Schill, F., 258, 273  
 Schimmel & Co., Ind., 631  
 Schink, N. F., 495  
 Schinz, H., 629, 631  
 Schleoten, A. W., 131, 145  
 Schlitter, E., 584, 590  
 Schlosser, M. E., 600  
 Schmal, A., 562, 570  
 Schmalfuss, H., 545  
 Schmerling, L., 339  
 Schmidt, 446, 452, 645, 651  
 Schmidt, C. T., 479, 480  
 Schmidt, L. K., 517  
 Schmidtmann, E., 161  
 Schmith, T., 567  
 Schmitt, C. G., 479, 480  
 Schmitt, F. O., 420, 433  
 Schmitz, 438  
 Schneider, 651  
 Schneider, K. W., 223, 233  
 Schneider, R., 562, 570  
 Schnell, H., 362, 366  
 Schnellen, C. G. I. P., 560, 570  
 Schoberl, A., 305, 308  
 Schoch, T., 497  
 Schoch, T. J., 528, 542  
 Schoenbach, E. B., 576  
 Schoenlaub, A., 192  
 Schofield, E. R., 668  
 Scholes, S. R., 261, 272  
 Scholl, I. M., 469  
 Schopf, J. M., 212  
 Schopmeyer, H. H., 495, 502  
 Schopp, E. T., 589  
 Schormüller, J., 535, 540, 543  
 Schrader, A. L., 530, 531, 542  
 Schroeder, A. L., 538, 543  
 Schroeder, C. R., 491  
 Schroeder, W. T., 542  
 Schroy, P. C., 365  
 Schuerch, C., 600  
 Schuftan, P. M., 31, 57, 181, 192  
 Schultz, A. S., 556, 569  
 Schulz, G. V., 345, 349, 350  
 Schulze, W. A., 417  
 Schunnacher, E. A., 163  
 Schumacher, J. C., 173, 191  
 Schundler & Co., F. E., 192  
 Schur, N. O., 368  
 Schurect, 282  
 Schurer, H., 416  
 Schuster, C. E., 468, 470, 474  
 Schwabe, K., 328  
 Schwartz, 532  
 Schwartz, F. F., 168, 190  
 Schwartz, H. A., 115, 125  
 Schwartz, S. L., 334  
 Schwarz, 648, 651  
 Schwarz, B., 550, 567  
 Schwarz, G., 524, 541  
 Schwarz, H. W., 22, 543  
 Schweigert, B. S., 568  
 Schweikert, 424, 433  
 Schweizer, R., 579, 581  
 Schwimmer, S., 551, 568  
 Scorah, R. L., 10  
 Scott, C. E., 463, 464, 474  
 Scott, D. H., 530, 531, 542, 545  
 Scott, G. P., 583  
 Scott, J. R., 404, 405, 416, 417  
 Scott, L. B., 593, 594  
 Scott, L. E., 542  
 Scott, W. D., 402, 416  
 Scott-Maxwell, I. S., 105, 124

**Scottish Reconstruction Committee,**  
197

- Scripture, P. N., 469  
 Seaber, 629  
 Seabright, C. A., 292  
 Seal, K. E., 262, 272  
 Seaman, W. C., 166, 190  
 Seaborn, W. E., 517  
 Sebe, Y., 632  
 Seebold, R. E., 430, 434  
 Seeger, D. R., 600  
 Seekles, L., 482, 483, 524, 541  
 Seeman, 296  
 Segre, A., 589  
 Seiberlich, J. K. H., 495  
 Seidel, C. F., 626, 632  
 Seiferle, E. J., 436  
 Seitz, F., 23  
 Sejersted, J., 160  
 Sekar, K. C., 400, 415  
 Selby, J. C., 116, 125  
 Selényi, 645, 651  
 Selfridge, R. R., 417  
 Seligman, R., 546, 566  
 Seligsberger, L., 429, 434  
 Selling, H. J., 500  
 Selman, 528  
 Selvig, W. A., 201, 213  
 Sem, M., 160  
 Semb, J., 600, 601  
 Sen, S. P., 172, 191  
 Senkus, M., 71  
 Serfass, E. J., 162, 428, 434  
 Sertl, J., 187, 193  
 Servais, P. C., 366, 417  
 Sessa, G. E., 163, 183, 193  
 Seyler, C. A., 197, 212  
 Seymour, D. E., 588  
 Seymour, R. B., 351, 632  
 Shabica, A. C., 586  
 Shaffer, M. C., 418  
 Shah, S. V., 254  
 Shanahan, C. E. A., 397, 398  
 Shands, H. L., 551, 567  
 Shane, S. J., 602  
 Shanley, E. S., 187, 194  
 Shantz, E. M., 579  
 Shapiro, M. M., 119, 126  
 Sharbaugh, A. H., 418  
 Sharpe, R. S., 117, 125  
 Sharples Chemicals, Inc., 71, 73  
 Shartsis, L., 261, 267, 272  
 Shaw, E., 454  
 Shaw, M. B., 333  
 Shaw, R. E., 411, 418  
 Shaw, T. M., 527, 542  
 Shawinigan Chemicals, 70  
 Shearon, W. H., 15, 417  
 Sheehan, J. T., 588  
 Shell Development Co., 73, 193, 364,  
 366, 376, 397, 617  
 Shellenberger, J. A., 24  
 Shelton, G. R., 292  
 Shema, B. F., 331  
 Shepherd, A. D., 544  
 Shepherd, R. G., 600, 618  
 Sheppard, J. R., 417  
 Sherman, G. D., 456, 457, 467, 469  
 Sherrington, 264  
 Sherwood, H. P., 653, 667  
 Sherwood, I. R., 509, 517  
 Sherwood, T. K., 17  
 Sheybany, H. A., 257, 271  
 Shibber, B. K., 145  
 Shimwell, J. L., 559, 569, 570  
 Shingler, G. P., 15  
 Shippee, E. D., 24  
 Shirley, H. T., 118, 121, 126  
 Shishkina, 643, 650  
 Shisterman, K. A., 119, 126  
 Shive, J. N., 162  
 Shive, W., 568, 581, 582  
 Shockley, W., 141, 142, 146  
 Shoeld, M., 193  
 Shoemaker, E., 570  
 Shokhor, I. N., 545  
 Shooter, R. A., 617  
 Short, W., 584  
 Shreve, R. N., 82, 94  
 Shrivastava, R. K., 254, 382  
 Shukis, A. J., 632  
 Shunk, C. H., 589  
 Shuttleworth, R., 162  
 Shuttleworth, S. G., 423, 424, 428, 433,  
 434  
 Shu-Tung Tu, 434  
 Sickels, J. P., 600  
 Siconolfi, C. A.  
 Siddiqui, S., 632  
 Siebert, C. H., 10  
 Siebert, C. L., 669  
 Siegler, E. A., 542  
 Sieling, D. H., 474  
 Siemens Electric Lamps & Supplies  
 Ltd., 194  
 Siemens Halske A.-G., 149  
 Siemers, G. F., 542  
 Sierichs, W. C., 254  
 Sievers, A. F., 621, 631  
 Signer, 313, 320  
 Silberman, Y. I., 191  
 Sillay, F. J., 334  
 Siller, C. W., 170, 191  
 Silman, H., 161  
 Silverman, A., 271, 273  
 Silverman, L., 161  
 Silverstein, M. S., 167, 190  
 Silverstein, R. M., 596  
 Silvis, S. J., 517  
 Simek, B. B., 201, 213  
 Simek, B. G., 197, 212  
 Simmonds, F. A., 329  
 Simon, J., 162  
 Simons, E. N., 24  
 Simonsen, (Sir) J., 627  
 Simpkinson, C. H., 192

- Simpson, C. R. H., 207, 214  
 Sims, C. E., 112, 125  
 Singer, F., 293  
 Singh, B. K., 254  
 Singh, C., 324  
 Singh, G. B., 632  
 Singh, R., 254  
 Singleton, W. S., 253  
 Sinnott, M. J., 10  
 Sirola, J., 162  
 Sisido, K., 596  
 Sivertz, C., 293  
 Skeen, J. R., 167, 190  
 Skelton, F. K., 161  
 Skerrey, E. W., 147  
 Skidmore, J. R., 25  
 Skinkle, 320, 321  
 Skinner, D. G., 293  
 Skolnik, H., 14  
 Skovsted, A., 556, 569  
 Slack, M. V., 604, 616  
 Slanetz, L. W., 491  
 Slansky, P., 382  
 Slate, G. L., 542  
 Slater, J. H., 205, 214  
 Slater, L., 211  
 Slater, V. W., 187, 194  
 Slator, A., 562, 570  
 Slavin, G., 491  
 Sleeth, C. K., 585  
 Slein, M. W., 553, 568  
 Slifkin, 648, 651  
 Slobodin, Y. M., 545  
 Slottman, G. V., 286  
 Slunder, C. J., 160, 647, 651  
 Smadel, J. E., 600  
 Smadel, J. S., 613, 618  
 Smart, J. A., jun., 132, 145  
 Smeaton, T., 204, 214  
 Smidh, L., 365  
 Smirnov, V. D., 212  
 Smirnova, 638, 650  
 Smith, 446, 447, 448, 452, 508, 638, 649  
 Smith, A. A., jun., 132, 145  
 Smith, A. E. W., 398  
 Smith, A. K., 253  
 Smith, A. L., 351, 480  
 Smith, C., 127  
 Smith, C. E., 255  
 Smith, C. S., 134, 145  
 Smith, E. G., 542  
 Smith, E. L., 582, 599, 604, 616  
 Smith, F., 517, 550, 567  
 Smith, F. G., 253  
 Smith, G. E. P., 418  
 Smith, G. H., 254  
 Smith, H. A., 416  
 Smith, H. L., 210, 215  
 Smith, I. W., 325  
 Smith, J., 294  
 Smith, J. A. B., 541  
 Smith, J. C., 219, 233  
 Smith, J. F. D., 29  
 Smith, J. J., 393  
 Smith, J. L. B., 631  
 Smith, J. M., 600  
 Smith, L. A., 565, 571  
 Smith, L. W., 24  
 Smith, M. H., 543  
 Smith, P. A., 571  
 Smith, P. V., 417  
 Smith, R. E., 418  
 Smith, R. M., 572, 577, 618  
 Smith, R. R., 348, 350  
 Smith, W., 598  
 Smith, W. A., 111, 116, 125  
 Smith, W. H., 529, 542  
 Smith, W. V., 348  
 Smock, A. W., 267, 272  
 Smook, R. M., 472, 542  
 Smoke, E. J., 292  
 Smoley, E. R., 217, 232  
 Smoliarenko, D. A., 109, 124  
 Smook, M., 77  
 Smythe-Holmwood, G. R. B., 476, 478  
 Snair, G. L., 121, 126  
 Snavely, C. A., 161  
 Snedden, H. D., 145  
 Snell, E. E., 559, 568, 569  
 Snell, F. D., 255  
 Snow, S. D., 544  
 Snowball, A. F., 169, 191  
 Snyder, F. M., 444  
 Snyder, H. R., 81, 94, 587  
 Sobel, A. E., 544  
 Soc. Anon de Matières Colorantes & Produits Chimiques Francolor, 83  
 Soc. Colorantes & Produits Chimiques Francolor, 75, 77  
 Soc. des Usines Chimiques Rhône-Poulenc, 73, 76  
 Society of Chemical Industry in Basle, 76, 84, 85, 86, 87, 88, 89, 91, 93, 97, 98, 100, 101, 375  
 Society of Glass Technology, 261  
 Socony-Vacuum Oil Co., Inc., 66, 73, 191  
 Soderberg, F. A., 331  
 Soderberg, K. G., 161  
 Soderlund, B., 212  
 Sognefest, P., 543  
 Solid Smokeless Fuels Federation, 62  
 Sollo, F. W., 665, 669  
 Solov'ev, 638, 639, 641, 650  
 Solowey, M., 527, 542  
 Solvay & Co., 192  
 Somerville, I. C., 429, 434  
 Sommer, K., 161  
 Sondhi, H. K., 627, 632  
 Soper, Q. F., 599  
 Sorkin, E., 588  
 Sortago, I., 571  
 Souci, S. W., 537, 545  
 Soule, E. C., 191  
 Sourlangas, S. S., 426, 434  
 Southern, 451

- Southwick, F. W., 471, 472  
 Southwick, P. L., 601  
 Spackman, W., jun., 393  
 Spanagel, 314, 321  
 Sparado, J. J., 253  
 Sparenburg, J., 623, 631  
 Sparrow, D. B., 347  
 Spaulding, E. H., 542  
 Speakman, J. B., 299, 307, 308, 313, 320  
 Spears, J. A., 53  
 Spedden, H. R., 127, 144  
 Speight, G. E., 119, 120, 126  
 Speiser, P., 590  
 Speitel, R., 584  
 Spence, 640, 642, 650  
 Spence & Sons, P., 73, 364  
 Spencer, R. D., 632  
 Spencer, R. S., 372, 382  
 Spencer-Strong, G. H., 291  
 Sperberg, L. R., 417  
 Sperry, P. R., 146  
 Spillsbury, J. F., 571  
 Spinks, J. W. T., 462, 464, 466, 469  
 Spinner, S., 267, 272  
 Spiro, P., 162  
 Spitze, L. A., 271, 273  
 Spohheim, H. W., 386  
 Spooner, C. E., 215  
 Sporn, P., 214  
 Sprague, G. F., 495  
 Sprague, V. G., 465, 469  
 Spring, F. S., 578, 588, 619  
 Springer, H. B., 505, 510, 518  
 Sproh, J. H., 106, 124  
 Sprung, 645, 651  
 Squibb & Sons, E. R., 616, 617  
 Squire, J. R., 366, 518  
 Sreenivasan, A., 430, 434, 549, 567  
 Srinivasan, V., 545  
 Stacey, M., 508, 517, 518, 519  
 Stack, O. R., 293  
 Stackleberg, M. V., 162  
 Stadie, U., 545  
 Stafford, R. L., 418  
 Stahel, W. M., 21  
 Stahl, B. F., 323  
 Stahl, C. W., 213  
 Stahl, J. C., 161  
 Stainsby, W. J., 254  
 Stair, R., 269, 273  
 Staley Manufacturing Co., A. E., 617  
 Standard Oil Development Co., 74, 75, 193, 221  
 Standard Telephones & Cables, Ltd., 193  
 Stanger, A., 27  
 Staniland, L. N., 477, 478  
 Stanley, A. R., 617, 651  
 Stannet, V., 370  
 Stansfield, R., 225, 227, 234  
 Stansly, P. G., 600, 618  
 Stanton, G. W., 342  
 Stanworth, J. E., 256, 258, 263, 268, 271, 272  
 Stareck, J. E., 123, 126  
 Stark, F. L., 479, 480  
 Stark, F. L., jun., 479, 480  
 Stark, W. H., 499, 551, 565, 566, 568, 571  
 Starnes, E. B., 443  
 Starnes, O., 443  
 Starr, G. H., 474  
 Stasiw, 637, 649  
 Staudinger, H., 360, 362, 366  
 Staudinger, J. J. P., 343, 346  
 Stauffer, R. A., 17, 133, 145, 649  
 Stavely, H. E., 618  
 Stebbins, R. B., 491  
 Steenberg, B., 314, 321, 330, 332, 334, 365  
 Steensberg, V., 539, 545  
 Stedehonder, P. L., 230, 234  
 Stedehonder, P. R., 219, 233  
 Steffen, H. C., 417  
 Stein, Hall & Co. Inc., 166, 190  
 Steinberg, R. H., 119, 126  
 Steiner, C. S., 7  
 Steiner, H., 218, 233  
 Steiner, W. A., 213  
 Steinhardt, R., 545  
 Stephanson, E., 333  
 Stephens, I. M., 538, 545  
 Stephens, L. G., 133, 145  
 Stephenson, R. E., 468, 470, 474  
 Sterbutzel, G. A., 364  
 Stern, A. C., 161  
 Sternitzki, H., 95  
 Stevels, J. M., 268, 273  
 Stevens, 643, 650  
 Stevens, C., 417  
 Stevens, H. P., 401, 415, 416  
 Stevens, R. J., 145  
 Stevens, W. H., 403, 416  
 Stevenson, 593  
 Stevenson, A. C., 77  
 Stevenson, E. P., 192  
 Steward, J. S., 491  
 Stewart, C. W., 506, 511, 517, 518  
 Stewart, E. D., 560, 570  
 Stewart, G. F., 521, 540, 541  
 Stewart, J., 262, 272, 293, 545  
 Stewart, J. L., 491  
 Stewart, R. S., 121, 122, 126  
 Stewart, W. D., 416  
 Stewart, W. S., 416, 472  
 Stewart, W. T., 193  
 Stickney, P. B., 373  
 Stillier, E. T., 575, 617  
 Stillson, G. H., 364  
 Stirling, A., 232  
 Stoa, T. E., 468, 470  
 Stock, E., 382  
 Stockel, O. F. C., 193  
 Stockholms Superfosfat Fabriks Aktiebolag, 77

Stockton, J. R., 568  
 Stoddard, C. K., 186, 193  
 Stoeger, H., 360, 366  
 Stoker, 451  
 Stokes, C. A., 417  
 Stokes, J. L., 298, 308  
 Stokstad, E. L. R., 580, 600, 601  
 Stoll, M., 632  
 Stone, I., 560, 564, 570, 571  
 Storch, H. H., 212  
 Storck, R., 554, 568  
 Storey, R. A., 19  
 Storm, R., 27  
 Stormont, N., 621, 631  
 Storrow, J. A., 20  
 Stott, 651  
 Stottman, G. V., 205, 214  
 Stotz, E., 542, 543  
 Stoves, J. L., 423, 433  
 Strachan, J., 314, 321, 368  
 Strain, D. E., 350  
 Strakhov, I. P., 429, 434  
 Straley, E. J., 491, 651  
 Strandskov, F. B., 554, 560  
 Strapp, R. K., 325  
 Strassle, 313, 320  
 Straub, F. G., 26  
 Straus, S., 349  
 Strausz, H. J., 627, 632  
 Strawbridge, D. J., 146  
 Streicher, L., 655, 668  
 Strickland-Constable, R. F., 202, 213  
 Stringfellow, 314, 317, 321  
 Strong, F. M., 543  
 Stuart, A. H., 161, 162  
 Stuart, N. W., 464  
 Stuart-Harris, C. H., 617  
 Stubbings, W. V., 255, 569  
 Stubblefield, C. J., 212  
 Stubbs, A. L., 544  
 Stumbo, C. R., 543  
 Stumpf, H. C., 146  
 Stumpf, P. K., 568  
 Sturton, R. I., 222, 233  
 Stussi, D., 525, 541  
 Subba Row, Y., 600, 601  
 Subrahmanyam, V., 568, 668  
 Sukov, M. K., 182, 193  
 Sullivan, H. M., 18  
 Sullivan, N. P., 599, 617  
 Sullivan, W. E., 293  
 Sumegi, L., 210, 215  
 Summer, 528  
 Sumner, J. A., 11  
 Sun, K. H., 256, 258, 271  
 Sunderland, E., 380, 382  
 Sundgren, A., 212  
 Sutcliffe, H. M., 323  
 Suter, E., 588  
 Sutherland, B. P., 192  
 Sutherland, G. B. B. M., 295, 308  
 Sutherland, J. E., 582  
 Sutherland, M. D., 632

Sutherland, R. E., 233  
 Sutra, R., 498  
 Suttle, J. F., 161  
 Sutton, D. A., 380, 382  
 Sutton, L., 261, 272  
 Sutton, R. R., 527, 542  
 Svahn, O., 116, 125  
 Svanhof, K., 540  
 Sventitsky, N. S., 118, 119, 126  
 Svetlik, J. V., 417  
 Swain, L. A., 254  
 Swain, M. L., 254  
 Swales, W. E., 491  
 Swallow, J. C., 16  
 Swanson, C. P., 483  
 Swarbrick, R., 193  
 Swatton, D., 162, 292  
 Swatezmann, F., 213  
 Sweet, A. T., 185, 193  
 Sweett, F., 27, 214  
 Swenson, E. A., 214  
 Swerdlow, 296  
 Swern, D., 385, 387  
 Swift, C. E., 254, 541  
 Swift, G., 518  
 Swift, P. N., 618  
 Switzer & Switzer, 648, 651  
 Sykes, J., 232  
 Sykes, W. O., 491  
 Sylvania Electric Products Inc., 194  
 Sylvester, J. C., 599  
 Symes, C. B., 451  
 Symmes, A. T., 599  
 Synan, J. F., 667  
 Synerholm, 436  
 Synowiedski, Z., 585  
 Syskov, K. I., 215

## T

Tabellini, M. T., 389  
 Tainton Products Co., 393  
 Talbott, C. P., 13  
 Tampa, J., 210, 215  
 Tanner, C. A., jun., 193  
 Tanner, C. C., 451  
 Tanzola, W. L., 25  
 Tapp, W. J., 77  
 Tarbell, D. S., 583  
 Tarjan, A. C., 479, 480  
 Tark, M. B., 668  
 Tarplev, E. C., 215  
 Tarr, H. L. A., 523, 540  
 Tatincloux, R., 262, 272  
 Tauber, H., 618  
 Taubken, H. R., 543  
 Taylor, 314, 321, 667  
 Taylor, A., 43  
 Taylor, A. L., 479, 480  
 Taylor, E. S., 555, 558, 569, 617  
 Taylor, G., 461, 464  
 Taylor, G. B., 362, 363, 366

- Taylor, J., 106, 124  
 Taylor, J. F., 9, 553, 568  
 Taylor, J. I., 491  
 Taylor, J. J., 481, 483  
 Taylor, M., 510, 517  
 Taylor, N. W., 265, 272  
 Taylor, R. C., 224, 233  
 Taylor, R. F., 77  
 Taylor, R. L., 177, 192  
 Taylor, V. T., 50  
 Taylor, W. K., 631  
 Taylor Tunncliffe Co., Ltd., 292  
 Teach, W. S., 384, 386  
 Teegan, J., 82  
 Teegan, M., 94  
 Teigland, M. G., 491  
 Tellez-Plasencia, 635, 644, 649, 650  
 Teltow, 637, 649  
 Tenhet, J. N., 451  
 Tennessee Eastman Corp., 374  
 Teply, L. J., 553, 568  
 Terhoeven, G. E., 669  
 Terrier, 497  
 Terry, J. H., 293  
 Tessier, H., 542  
 Textor, C. K., 325  
 Thacker, C. M., 191  
 Thacker, F. B., 205, 214  
 Thain, E. M., 621, 631  
 Thau, A., 41  
 Thaysen, A. C., 538, 545, 558, 569  
 Theis, E. R., 427, 434  
 Thistle, M. W., 542  
 Thole, F. B., 223, 233, 234  
 Thom, G. V., 20  
 Thoman, R., 416  
 Thomas, E. H., 653, 667  
 Thomas, J., 112, 125  
 Thomas, T. F., 11, 207, 214  
 Thomas & Baldwin Ltd., R., 155  
 Thomason, 541  
 Thompson, A. A., 472  
 Thompson, C. L., 288  
 Thompson, F. B., 483  
 Thompson, F. C., 125, 140, 146  
 Thompson, H. L., 547, 566  
 Thompson, J. B., 192  
 Thompson, J. W., 479, 480  
 Thompson, P. F., 131, 145  
 Thompson, R. C., 145  
 Thompson, W. G., 110, 114, 125  
 Thomson, R. M., 161  
 Thomson, T. R., 496  
 Thon, N., 161  
 Thonberg, M. W., 229  
 Thorn, J. A., 617  
 Thornberry, H. H., 617  
 Thorne, C. B., 618  
 Thorne, G., 479, 480  
 Thornhill, R. S., 123, 126, 393  
 Thornton, A. A., 494  
 Thornton, G. D., 465, 469  
 Thorp, W. T. S., 491  
 Thorsen, G., 518  
 Thring, M. W., 32, 205, 209, 214, 215  
 Thrower, R. D., 470  
 Thunaeus, H., 547, 566  
 Thunnauer, H., 293  
 Thurlby, E. G., 116, 125  
 Thurston, A. P., 365  
 Tiedjens, V. A., 463, 464  
 Tiedman, W. D., 569  
 Tiedmann, H., 161  
 Tilbury, W. G., 212  
 Tilton, L. W., 263, 272  
 Tingle, E. D., 228, 234  
 T'ing-Sui Ké, 136, 146  
 Tinus, K., 365, 371  
 Tippo, O., 393  
 Tiselius, A., 508, 517  
 Tishler, M., 586, 587  
 Titanium Alloy Manufg. Co., 193, 194  
 Titus, E., 576, 618  
 Tiwari, L. D., 254  
 Todhunter, E. N., 543  
 Toenges, A. L., 212  
 Tokich, J. L., 135, 145  
 Tollert, 639, 650  
 Tolliday, J. D., 428, 431, 434  
 Tolstopyatova, A. A., 350  
 Tomashov, N. D., 160  
 Tomlinson, G. H., 571  
 Tomlinson, J., 433  
 Tomlinson, T. G., 668  
 Toms, B. A., 440, 478  
 Tomula, E. S., 175, 191  
 Tool, A. Q., 259, 263, 271, 272  
 Topley, E., 366  
 Topper, H. H., 382  
 Topschiev, A. V., 220, 233  
 Torgeson, D. R., 175, 191  
 Tornow, P. A., 621, 631  
 Torrey, R. M., 217, 232  
 Toth, S. J., 469  
 Townend, 317, 321  
 Townend, D. T. A., 49  
 Townend, F. S., 46  
 Towers, J., jun., 136, 146  
 Townsend, A. J., 207, 214  
 Toy, A. D. F., 387  
 Traill, 313, 320  
 Traub, R., 600  
 Traube, S. B., 293  
 Trautz, O. R., 145  
 Treadway, R. H., 493  
 Treibs, W., 626, 632  
 Treloar, L. R. G., 405, 411, 416, 418  
 Trenner, N. C., 601  
 Trenner, N. R., 574  
 Tressler, C. K., 543  
 Trillat, J. J., 227, 234  
 Tripp, D., 478  
 Tritton, S. N., 537, 544  
 Trivedi, S. A., 329  
 Trivelli, 638, 649  
 Troember, A. P., 663, 669

Trofimov, V. I., 631  
 Troiano, A. R., 135, 145  
 Trolle, B., 562, 570  
 Trombe, F., 135, 145  
 Trommsdorf, E., 345  
 Tromp, L. A., 518  
 Trotter, F. M., 198, 212  
 Troyan, J. E., 417  
 Truman, J. E., 121, 126  
 Truog, E., 474  
 Trusov, 649  
 Tucker, E. B., 585  
 Tucker, H. H., 301, 308  
 Tucker, W. H., 16  
 Tucker, W. R., 375  
 Tudor, P., 478  
 Tugov, I. I., 212  
 Tukey, H. B., 478  
 Tulasne, R., 617  
 Tullar, B. F., 586  
 Turk, L. M., 455  
 Turley, H. G., 429, 434  
 Turnbull, L. A., 212  
 Turncock, L. C., 364  
 Turner, H. D., 334  
 Turner, J. N., 429, 434  
 Turner, N. C., 499  
 Turner, R. B., 590  
 Turner, W. E. S., 261  
 Turnock, L. C., 193  
 Turtle, 449, 452  
 Tusson, J. R., 167, 190  
 Tutton, M. J., 535, 544  
 Twele, C., 163  
 Twyman, F., 262  
 Tyrer, D., 74  
 Tyrer, H. G. P., 516  
 Tyrie, W. R., 357, 365  
 Tyrrell, H. J. V., 655, 667

## U

Udupa, H. V., 79  
 Ufimtsev, V. M., 82, 94  
 Uhlig, H. H., 119, 126  
 Uhrig, I. J., 491  
 Ujhelyi, C., 517  
 Ukimoto, I., 212  
 Ulrich, J., 534, 543  
 Ulrich, R., 536, 544  
 Umberger, 651  
 Umbreit, L. E., 569  
 Umbreit, W. W., 568  
 Underkoffler, L. A., 565, 571  
 Underwood, A. F., 162  
 Underwood, A. J. V., 14  
 Unilever, 318  
 United Chromium, Inc., 161  
 United States Bureau of Mines, 128,  
 144, 145, 152  
 U.S. Department of Agriculture, 322,  
 359, 365, 374

U.S. Rubber Co., 75, 366, 386  
 U.S. Secretary of Agriculture, 385, 386  
 Universal Oil Products Co., 70, 73, 231  
 Untermohlen, W. P., 369  
 Upjohn Research Labs., 374  
 Uppal, I. S., 493  
 Urion, A., 173, 191  
 Urion, E., 549, 560, 563, 567, 570, 571  
 Usines de Melle, 71  
 Ustalova, Z. A., 119, 126

## V

Vaaler, 647, 651  
 Vahrman, M., 215  
 Vail, G. E., 540  
 Valente, R., 571  
 Valentiner, S., 146  
 Vallen, 649, 651  
 Vallin, S., 332  
 Van Allen, A. M., 325  
 Van de Erve, A., 253  
 Vander Noot, G. W., 486, 488  
 Van Dillewijn, C., 512, 518  
 Van Dusen, 648, 651  
 Van Goor, W. R., 382  
 Van Hook, A., 519  
 Van Lanen, J. M., 571  
 Vannoy, W. G., 388, 393  
 Vanselow, 636, 649  
 Van Slyke, D. D., 561, 570  
 Varde, M. S., 178, 192  
 Varela, G., 600  
 Vasil'ev, G. A., 383  
 Vaskevich, D. N., 365  
 Vassiliou, B., 292  
 Vastagh, G., 544  
 Vaughn, T. H., 255  
 Vavich, M. G., 543  
 Veersen, G. J. van, 417  
 Veisseyre, R., 541  
 Veldhuis, M. K., 532, 543  
 Veldhuizen, H. van, 563, 571  
 Velick, S. F., 568  
 Velz, C. J., 660, 668  
 Vendrely, R., 617  
 Venezia, M., 542  
 Venkataraman, 321  
 Vennesland, K., 588, 618  
 Ventre, E. K., 517  
 Vermaas, 311, 320  
 Vermonde, C., 366  
 Vernon, C. C., 499  
 Vernon, T. R., 541  
 Vernon, W. D., 547, 566  
 Vero, E., 555, 568  
 Verzele, M., 548, 567  
 Vickerstaff, 315, 316, 317, 321  
 Vickery, H. B., 561, 570  
 Victor Chem. Works, 387  
 Vidal, R. E., 202  
 Viel, G., 450

Viertel, O., 255  
 Vigers, T. W., 179, 192  
 Vignolo, R. L., 555, 569  
 Vigue, R. F., 491  
 Vinal, G. W., 163  
 Vincent, 118  
 Vincent, C. L., 472  
 Vincent, G. P., 300, 307  
 Vincke, E., 545  
 Vinton, C., 543  
 Vinton, C. B., 516  
 Virden, C. J., 562, 570  
 Virtanen, A. I., 539, 545  
 Visking Corp., 398  
 Vittum, 646, 651  
 Vivian, J. E., 171, 191, 326  
 Vix, H. L. E., 253, 416  
 Vlach, 638, 649  
 Vloten, G. W. van, 442  
 Voce, E., 140, 146  
 Vogel, R., 146  
 Vogl, A., 571  
 Vogt, E. G., 7  
 Voigt, U., 12  
 Vokes, F. C., 668  
 Volcani, B. E., 559, 570  
 Volkovich, 460, 464  
 Volpert, G. R., 422, 433  
 Volz, F. E., 544  
 Voromin, N. A., 212  
 Vose, W., 292  
 Vosskühler, H., 132, 145  
 Vought, F. A., 504, 516  
 Vroman, D. F., 491

## W

Waber, J. T., 114, 125  
 Wachs, H., 632  
 Wacks, 436  
 Waddell, C. W., 505, 516  
 Waddey, W. E., 345  
 Wade, C. F., 209, 215  
 Wade, W., 366  
 Wadhvani, T. K., 668  
 Wadley, J. M., 539, 545  
 Wadman, W. H., 517  
 Wadsworth, D. V., 518  
 Wadsworth, F. T., 396, 397  
 Wager, H. G., 543  
 Waggoner, J. A., 493  
 Wagner, H., 389  
 Wagner, J. R., 543  
 Wagner, R. M., 161  
 Wagner, W. F., 212  
 Wakeham, H., 12  
 Wakeman, D. W., 146  
 Waksman, S. A., 575, 617, 618  
 Waley, S. G., 295, 308  
 Walker, A. D., 818  
 Walker, A. R. P., 529, 542  
 Walker, H. G., 601

Walker, J., 581  
 Walker, J. F., 364  
 Walker, J. G., 25, 655, 668  
 Walker, R., 47, 54  
 Walker, T. K., 548, 555, 559, 567, 569, 570  
 Walker, V., 202, 213  
 Walkley, A., 482, 483  
 Wallace, A., 469  
 Wallace, E. L., 369  
 Wallace, G., 213  
 Wallace, H. D., 470, 545  
 Wallace, L. R., 484, 487  
 Wallace, T., 463, 464  
 Wallbank, A. W., 163  
 Waller, C. W., 600, 601  
 Waller, R. J., 290  
 Wallerstein, J. S., 568  
 Wallerstein, L., 564, 571  
 Wallquist, G., 116, 125  
 Walls, L. P., 491  
 Walagrove, E. R., 233  
 Walsh, A. D., 226, 234  
 Walter, 319, 321  
 Walters, S. H., 119, 126  
 Waltz, J. E., 314, 321, 366  
 Wandless, A. M., 211  
 Wannow, 312, 320  
 Ward, F. N., 483  
 Ward, H. F., 194  
 Warner, D. T., 587  
 Warshowsky, B., 398, 570  
 Washburn, H. W., 233  
 Wastfund, C., 291  
 Waters, W. A., 80, 93  
 Watkins, W. J., 439, 451, 563, 571  
 Watkins, W. W., 366  
 Watkinson, E., 205, 214  
 Watson, A. J., 542  
 Watson, D. W., 524, 541  
 Watson, J., 295, 308  
 Watson, J. M., 598  
 Watson, P. D., 385, 387  
 Watson, W. F., 351  
 Watson, Y., 388  
 Watt, J., 176, 192  
 Watts, B. M., 537, 544  
 Watts, P. S., 491  
 Wearmouth, W. G., 364  
 Weatherford, J. A., 416  
 Weatherhead, T. D., 229  
 Weatherwax, P., 498  
 Weaver, C., 81, 94  
 Weaver, L. R., 454  
 Webb, E. C., 552, 568, 635, 636, 649  
 Weber, C. G., 333  
 Weber, H. C., 32  
 Webster, G. R., 109, 124  
 Weed, F. G., 395  
 Weedman, J. A., 181, 192  
 Wegner, H., 502  
 Weibel, S. R., 669  
 Weidemann, A. G., 467, 469

- Weidinger, 31', 320  
 Weigel, W., 371  
 Weil, B. H., 219, 231, 233, 234  
 Weil, R. F., 162  
 Weinert, P. C., 222, 233  
 Weinrub, L. G., 179, 192  
 Weinstein, P., 524, 541  
 Weir, C. E., 431, 434  
 Weisblat, D. I., 600  
 Weiss, P., 596  
 Weiss, R. H., 668  
 Weiss, S., 42  
 Weiss, Z., 600  
 Weissberger, 645, 646, 651  
 Weissenberg, K., 404, 416  
 Weisz, R. S., 163  
 Weizmann, C., 69, 232  
 Welb, T. L. B., 26  
 Welch, J. C., 366  
 Weller, K., 162  
 Wellinger, K., 27  
 Wellm, J., 524, 541  
 Wells, J. H., 64  
 Wells, R. R., 144, 145  
 Wells, R. S., 194  
 Welsh, M., 491  
 Wendland, G., 527, 536, 541, 544  
 Wendling, 382  
 Wendon, G. W., 389  
 Wenzl, H., 328  
 Werkman, C. H., 558, 569  
 Werner, J., 77  
 Werner, R. R., 340  
 Wertham, J. S., 393  
 Wessely, 596  
 West, C. J., 518  
 West, G. A. V., 20  
 West, H. L., 228, 234  
 Westcott, J. F., 293  
 Westerman, A. B., 146  
 Westerman, B. D., 540  
 Western Electric Co., Inc., 193, 350  
 Westinghouse Corp., 155  
 Westinghouse Electric International Co., 365  
 Weston, 319, 321  
 Weston, W. A. R. D., 467, 469  
 Westvaco Chlorine Products Corp., 167, 190  
 Westwater, J. W., 382  
 Wettstein, A., 589  
 Weyerts, 636, 649  
 Weyl, W. A., 259, 265, 270, 272, 273  
 Whaley, F. R., 192  
 Wheeldon, G. E., 28  
 Wheeler, W. H., 5, 187, 194  
 Whelan, W. J., 499  
 Whetstone, R. R., 364  
 Whiffen, A. J., 618  
 Whinfield, J. R., 361, 366  
 Whistler, R. L., 498  
 Whitaker, A. E., 376  
 White, 646, 651  
 White, A. C. G., 558, 569  
 White, A. G., 20  
 White, C. K., 326  
 White, E. P., 481, 483  
 White, H. J., 600  
 White, J., 292, 558, 569  
 White, J. C. D., 541  
 White, N. C., 173  
 White, P. H., 334  
 White, R. O., 512, 518  
 White, R. R., 7  
 White, W. C., 16  
 White, W. E., 193  
 Whitehead, C. W., 599  
 Whitehead, H. R., 541  
 Whitmore, R. A., 535, 544  
 Whitely, W. A., 564, 571  
 Whitmore, F. C., 219, 233  
 Whitmore, L. M., 432, 434  
 Whitnall, 451  
 Whitney, J. E. S., 365  
 Whitney, R. P., 171, 191, 326, 327  
 Whitson, M. T. B., 657, 668  
 Whittaker, 318, 321  
 Whittaker, C. W., 483  
 Whittaker, H., 187, 194  
 Whittenberger, R. T., 500  
 Whittmann, J., 145  
 Whorlow, R. W., 405, 417  
 Wiame, J. M., 557, 569  
 Wick, W. C., 107, 108, 124  
 Wicke, E., 12  
 Wickerham, L. J., 557, 569  
 Victorin, C. G., 139, 146  
 Widell, T., 212  
 Wiederhold, 636, 649  
 Wiegand, R. V., 233  
 Wiegand, W. B., 408  
 Wiegel, R., 279  
 Wiehe, P. O., 518  
 Wieland, P., 602  
 Wiener, S., 554, 568  
 Wigga, P. W. O., 219, 233  
 Wiggins, L. F., 515, 516, 519  
 Wijga, P. W. O., 230, 234  
 Wilcock, 317, 321  
 Wilcox, J. C., 482, 483  
 Wilcox, M. S., 544, 545  
 Wild, R., 105, 124  
 Wilde, J. H. K., 491  
 Wilder, 646, 651  
 Wilds, A. L., 589, 593  
 Wiley, H. F., 233  
 Wiley, R. H., 345, 362, 366, 386  
 Wilham, C. A., 518  
 Wilharm, G., 558, 569  
 Wilhelm, R. H., 7  
 Wilkes, S. H., 20  
 Wilkin, M., 541  
 Wilkinson, C. S., 418  
 Wilkinson, S., 600, 618  
 Willard, C. J., 323  
 Willcox, O. W., 181, 192

- Willett, 504  
 Willey, E. J. B., 505, 516  
 Willey, L. A., 146  
 Williams, 449, 452  
 Williams, C. D. B., 161  
 Williams, C. G., 230, 234  
 Williams, E. G., 366  
 Williams, E. L., 491  
 Williams, F. J., 387  
 Williams, G. C., 13  
 Williams, H., 537, 544  
 Williams, J. F., 561, 570  
 Williams, K. A., 381  
 Williams, S. J. D., 53  
 Williams, V., 518  
 Williams, W. J., 117, 126  
 Williams, W. L., 568  
 Williams (Hounslow), Ltd., 87  
 Williamson, 262  
 Williamson, J. E., 128, 145  
 Williamson, R. H., 52  
 Williamson, R. V., 364  
 Williamson, W. O., 275, 291  
 Willihnganz, E., 163  
 Willis, J. M., 82, 94  
 Willkie, H. F., 565, 566, 571  
 Willson, K. S., 161  
 Wilmanns, 641, 650  
 Wilmot, J. W., 567  
 Wilson, 440, 441, 451  
 Wilson, C., 610, 617, 641, 650  
 Wilson, D. J., 567  
 Wilson, E. A., 416  
 Wilson, F. H., 139, 146, 192  
 Wilson, H. F., 476, 478  
 Wilson, I., 451  
 Wilson, J. K., 443  
 Wilson, K., 368  
 Wilson, L. M., 49  
 Wilson, P. J., 64  
 Wilson, R. A., 22, 167, 190  
 Wilson, R. E., 123, 126  
 Wilson, S. G., 491  
 Wilson, W. M., 617  
 Wiltshire, W. A., 331  
 Windaus, 583  
 Windenberg, D. F., 27  
 Winding, C. C., 9  
 Winge, O., 556, 569  
 Wingfoot Corp., 72  
 Winheim, 427, 434  
 Wink, W. A., 335  
 Winkler, C. A., 364  
 Winkler, L. E., 364  
 Winks, 261  
 Winsor, C. E., 668  
 Winstanley, A., 212  
 Winsten, W. A., 576, 618  
 Winter, A. R., 527, 541  
 Winter, G., 387, 393  
 Winter-Klein, A., 256, 271  
 Winteringham, 447, 448, 449, 452  
 Wintersteiner, O., 575, 617  
 Winthrop-Stearns, Inc., 617  
 Winton, 641, 650  
 Wischhusen, J. F., 463, 464  
 Wisconsin Alumni Research Founda-  
 tion, 165, 190  
 Wise, E. C., 600  
 Wiss, O., 587  
 Withnell, I., 668  
 Witkop, B., 584  
 Wittbecker, E. L., 366  
 Wittner, 304, 308  
 Wittwer, S. A., 473  
 Wocasek, J. J., 253  
 Wodicka, V. O., 545  
 Wogburn, R. S., 451  
 Wohlers, H. C., 600  
 Wokes, F., 537, 544, 554, 568  
 Wolf, B., 482, 483  
 Wolf, D. E., 601  
 Wolf, F. T., 605, 617  
 Wolf, K., 410, 418  
 Wolf, M. J., 498  
 Wolfrom, M. L., 508, 517, 575, 576, 618  
 Wolstenholme, S., 431, 434  
 Wood, A. P., 359, 365, 464  
 Wood, L. K., 455, 456  
 Wood, T. R., 601  
 Wood, W. A., 113, 125  
 Wood, W. S., 187, 194  
 Woodward, 441  
 Woodland, 643, 650  
 Woodman, H. E., 486, 488, 539, 545  
 Woodmanasee, C. W., 536, 544  
 Woodruff, H. B., 617  
 Woodthorpe, T. J., 566, 571  
 Woodward, R. B., 583, 584  
 Woodward, T. E., 600  
 Woody, E., 618  
 Woolley, D. W., 568  
 Woolley, R. L., 141, 146  
 Work, L. T., 204, 213  
 Wormell, R. L., 305, 308  
 Wray, R. I., 389  
 Wright, 447, 452, 647, 651  
 Wright, B. A., 420, 433  
 Wright, E. P., 228, 234  
 Wright, F. H., 517  
 Wright, G. F., 396, 397  
 Wright, G. G. H., 559, 570  
 Wright, H. F., 600  
 Wright, J., 101  
 Wright, L. T., 618  
 Wright, S. E., 632  
 Wright, W. G., 20  
 Wruck, M., 543  
 Wulfekuhler, A. F., 517  
 Wulff, H. D., 631  
 Wyckoff, R. W. G., 302, 308  
 Wyeth, Inc., 617  
 Wyllie, M. R. J., 161  
 Wynne, J. N., 211  
 Wysong, W. S., 147  
 Wyss, O., 554, 568

## Y

Yagol, N., 7  
 Yampol'skii, 639, 641, 650  
 Yancey, H. F., 213  
 Yannaquis, N., 137, 146  
 Yanovsky, E., 519  
 Yarborough, J. H., 491  
 Yarza, A. A., 254  
 Yatheraja, A. R., 506, 516  
 Yeager, A. F., 473  
 Yeager, B. J., 26  
 Yearwood, R. D. E., 506, 516  
 Yee, L. V., 464  
 Yeh, H. L., 469  
 Yellott, J. I., 207, 214  
 Yelton, E. B., 29  
 Yeo, 460  
 Yeo, D., 186, 193  
 Yeo, M. L., 207, 214  
 Yerkes, L. A., 145  
 Yntema, L. F., 162  
 Yoder, J. D., 26  
 Yoke, G. R., 212  
 Yorston, F. H., 328  
 Yoshino, K., 372  
 Yothers, M. A., 440  
 Young, E. G., 350  
 Young, L. I., 214  
 Young, T. E. B., 212  
 Young, W. S., 224, 233  
 Youngken, H. W., 497, 632  
 Youmans, G. P., 491, 618  
 Yule, 646, 651

Yun Pei Sun, 442  
 Yutzy, 449

## Z

Zabawsky, Z., 270, 273  
 Zachlin, A. C., 163  
 Zahm, W., 602  
 Zahn, H., 298, 307, 308, 313, 320  
 Zairnis, E. J., 597  
 Zajic, 596  
 Zamiatina, V., 366  
 Zander, J. M., 293  
 Zankl, W., 49  
 Zapffe, C. A., 114, 125  
 Zarembo, K. S., 198, 212  
 Zechmeister, L., 508, 517  
 Zeh, 651  
 Zeleny, L., 529, 542  
 Zeller, G., 69  
 Zeltner, J., 69  
 Zerban, F. W., 509, 514, 517, 519  
 Zhadanovskii, K. T., 213  
 Zhurin, A. I., 161  
 Zieman, W. E., 10  
 Ziifle, 310, 320  
 Zimmerman, E. W., 418  
 Zimmerman, G., 544  
 Zimmermann, P. W., 472, 535  
 Zmihorski, E., 161  
 Zuch, T., 543  
 Zuckerman, R. C., 517  
 Zussmann, H. W., 32

# SUBJECT INDEX

## A

A.D.5 paste, 206  
 Abattoirs, waste waters from, 663  
 Acenaphthalene, polymerisation of, 347  
 Acetaldehyde, polymerisation of, 348  
 Acetic acid from ethanol, 69  
*Acetobacter* in beer and yeast, 559  
*Acetobacter suboxydans*, 559  
 Acetone, synthesis of, 70  
 3- $\beta$ -Acetoxyandrost-5-ene-7:17-dione, 592  
 (3-Acetylthio) propan-1-al, 71  
 Acids, carboxylic, 69  
   fatty, esterification of, 239  
   from paraffin wax, 218  
   separation of, 239  
   separation and determination of, by chromatography, 249  
   vinyl esters of, 384  
   waste, neutralisation of, with limestone, 177  
 Acetic acid, production and determination of, 514  
*Acorus calamus*, essential oil from, 623  
 Acraldehyde, manufacture of, 71  
 Acrylic acid, 69  
   synthesis of, 344  
   esters, 346  
 Acrylonitrile, polymerisation of, with vinyl chloride, 408  
   synthesis of, 347  
 Actidione, 578, 614  
 Acylaminophthaloylacidones, 98  
 Adhesion, physics of, 270  
 Adhesives in industry, 414  
   melamine, for plywood, 360  
   phenolic resins as, 357  
 Adipic acid, 69  
 Adsorption of gases, 12  
 Aerators, 660  
 Aerosols, 439, 478  
   storage of, in metal containers, 437  
 Aerosporin, 576, 615  
*Agathosma gnidoides*, essential oil from, 623  
 Agriculture, fuel utilisation in, 207  
   radio-active tracers in, 462  
 Air, determination of, in beer and worts, 560  
   *See also* Atmosphere  
 Aircraft, lacquers for, 394  
   spraying from, 440, 477  
 Alcohol, determination of, in potable spirits, 561  
   from maize starch, 502  
   from molasses, 509

Alcohol—*continued*  
   injection devices for, as fuel, 515  
   production of, 565  
 Alcohols, 68  
   determination of, in essential oils, 629  
   polyhydric, acetylation of, 550  
 Aldehydes, 70  
 Aldolase, 552  
 Aldoses, methylated, determination of, 550  
 Aliphatic compounds from petroleum, 217  
 Alkali hydroxides, purification of solutions of, 176  
   selenides, production of, 183  
   sulphides, anhydrous, production of, 176  
 Alkaline-earth aluminates, 180  
   hydrides, 180  
   oxides, 180  
 Alkaloids, curare, 585  
   strychnos, 582  
 Alkanolamines, production of, 72  
 Alkylamines, 71  
 Alkylation, 219  
 Alligator weed on sugar cane, 512  
 Alloys, acid-resistant, 29  
   age-hardened, transient creep in, 141  
   constitution of, 137  
   electro-deposition of, 155  
   heat-resisting, 144  
   internal stresses in, 113  
   non-ferrous, heat-treatment of, 115  
   precious-metal, stress corrosion of, 144  
 Allyl chloride, 67  
 Methacrylate, polymerisation of, 347  
   starch, 496  
   sucrose, 514  
 Alum, production of, 185  
 Alumina. *See* Aluminium oxide  
 Aluminates, 180  
 Aluminium alloys, corrosion protection of, 143  
   degassing of, 133  
   with high Young's modulus, 140  
   and its alloys, casting of, 132  
   in the food industry, 534  
   coating of cellophane with, 17  
   containers for hydrogen peroxide, 187  
   -copper-magnesium-zinc alloys, 138  
   corrosion of, in lithography, 648  
   electrometallurgy of, 148  
   for bakery equipment, 529  
   in pigments, 389  
   oxide, production, properties, and recovery of, 183  
   sintering of, 286

- Aluminium—*continued*  
 —magnesium alloys, corrosion in, 143  
 grain growth in, 136  
 —magnesium-manganese-zinc alloys, 138  
 —magnesium-zinc-chromium alloys, 138  
 —manganese alloys, grain growth in, 136  
 —manganese-cadmium alloys, 137  
 —manganese-copper alloys, 137  
 —manganese-nickel alloys, 137  
 mechanism of slip in, 141  
 production of, 129  
 refining of, 129  
 single crystals of, 137  
 soaps, 250  
 —sodium alloys, 138  
 sodium fluoride, 171  
 —zinc-manganese alloys, 137
- Anbergris, 629
- Amines and their derivatives, 74  
 aromatic, acetylation of, 74
- Amino-acids, bacteria fermenting, 559  
 preparation of, 72  
 synthesis of, 585
- 2-Aminoazobenzene, 81
- Aminoazo-compounds, 81
- Aminobenzthiazoles, 77
- $\epsilon$ -Aminocapro lactam, synthesis and polymerisation of, 362
- 2-Aminodiphenyl sulphones, 75
- 2-Amino-4-hydroxy-6-methylpteridine, 581
- 2-Amino-4-methylpyrimidine, 76
- Aminophenols, preparation of, 74
- Aminoplastics, degradation of, 358
- 2-Aminopyrazines, 76
- 2-Aminopyrroline 1-oxides, 76
- p*-Aminosalicylic acid, 588
- 2-Aminothiazole, 530
- Ammonia, anhydrous, as fertiliser, 459  
 catalytic oxidation of, 165  
 disposal of, from coke-oven plants, 55  
 dissociated, for hydrogenation of fats and oils, 238  
 production of, 164
- Ammonium bisulphite in pulping, 327  
 chloride, recovery of, 175  
 compounds, quaternary, as antiseptics, 555  
 nitrate, determination of, in fertilisers, 480  
 crystallisation of, 166  
 fertilisers, explosions due to, 166  
 production of, 165  
 sulphate, production of, 165
- Amylase activity, determination of, 497  
 $\alpha$ - and  $\beta$ -Amylases, action of, on starch, 549  
 determination of, 550  
 in bread making, 528  
 purification of, 551
- Amylopectin, separation of, from amylose, 497
- Amylose, determination of, in starch, 498  
 preparation of, 495  
 separation of, from amylopectin, 497
- Amyloses, biological synthesis of, 494
- n*-Ampylenicillin, 610
- Anaemia in swine due to copper deficiency, 539  
 pernicious, anti-factor for, 582
- Analysis, metallurgical, spectrographic, 118
- Anethole, 622
- Aneurin, distribution of, in cereal grains, 553
- Aniline-*D*-ribopyranoside, 74
- Animals, damage to, by insecticides, 441  
 nutrition of, 484
- Aniseed oil, 622
- Anisole, preparation of, 73
- Anodes, graphite, 159
- Anthraquinone dyes, 96
- Anthratube, 206
- Antiarigenin, 590
- Antiarins, 590
- Antiaris toxicaria*, 590
- Antiarose, 590
- Antibiotics, 136, 573, 603, 613  
 peptides as, 553
- Anti-bronzing agents, 638, 644
- Anti-foggants, 637, 638, 644
- Anti-fouling compositions, 123, 392  
 chlorinated rubber for, 406
- Antioxidants, 242
- Antiseptics, new, for beer, 554
- Antrycide, 599  
 in veterinary practice, 490
- Antrypol, 599
- Aphids, control of, 436, 440
- Apple juice, 531  
 slices, "firming" of, 531
- Apples, canning of, 535  
 control of scald in, 530  
 thinning of, growth substances for, 471  
 zinc deficiency effects in, 473
- Arsenic, determination of, in brewing materials, 561
- Artemisia*, essential oils from, 623
- Artemisia absinthium*, essential oil from, 622
- Artichokes, alcohol from, 565
- Aryl alkyl ethers, preparation of, 74
- Ascaridole, determination of, 630
- Ascaris lumbricoides*, 661
- Ascorbic acid, determination of, 537  
 in fruits and vegetables, 472  
 in fruit syrups and jams, 536  
 loss of, in processing vegetables, 532
- Asparagus, canning of, 535
- Aspergillie acid, 578  
 structure of, 616
- Asphaltenes from coal, 199
- Atmosphere, pollution of, 207

Aureomycin, 566, 613  
 Austenite, decomposition of, 116  
 Axerophthene, 579  
 Azeotropic mixtures, distillation of, 14  
*cis*-Azobenzene, structure of, 81  
 Azo-compounds, absorption spectra and structure of, 82  
   containing boronic acid groups, 81  
 Azo-couplers, 648  
 Azo-dyes, 80  
   bisulphite compounds of, 82  
   diazo-components for, 75  
   iodine-containing, 82  
   metallisable, 84  
   reactions of, with copper salts, 83  
 Azoic dyes, coupling components for, 77  
 Azulenes, 626

## B

BHC, toxicity of, to plants, 441  
 Bacilli, tubercle, in sewage, 661  
 Bacillomycin, 614  
*Bacillus aerosporus* and *polymyxa*, 615  
 Bacitracin, 577, 614  
 Bacon, Canadian Wiltshire, storage of, 534  
   canned, bacteria in, 534  
   treatment of, with anti-oxidants, 539  
 Bacteria, coliform, determination of, in water, 653  
   effect of freezing on, 536  
   in bate liquors, 432  
   in raw sugar, 513  
   iron, 332, 653  
   sulphate-reducing, in sewers, 659  
 Bagasse, sugar cane, 510  
 Baking industry, 527  
 Bamboo for paper and pulp manufacture, 324  
 Bananas, Panama disease of, 614  
   wild, starch from, 495  
 Barges, ventilation of, used for fumigation, 445  
 Barium cyanide, 178  
   dicyanamide, 178  
   nitrate, production of, 178  
   production of, vacuum, 17  
   silicates, activated, phosphorescence of, 178  
   zirconium silicate to increase shock resistance, 279  
 Bark, removal of, 325  
 Barley, damage to, 547  
   germination of, 553  
   malting of, for brewing, 546  
   marketing of, 547  
   "take-all" infection in, 467  
 Barytes, production and uses of, 178  
*Basia longifolia*, essential oil from, 623

Bate liquors, bacteria in, 432  
 Batteries, storage, grids and plates for, 160  
 Beating, 329  
 Beech-wood, pulping of, 326  
 Beer, analysis of, 560  
   biological sampling of, 565  
   bottled, effect of air on, 564  
   brewing of, 562  
   casks for, 563  
   disinfection, preservation, and sterilisation of, 554  
   filtration of, 563  
   lager, fermentation of, 562  
   nitrogen fractions of, 564  
   preservative effect of hops on, 548  
   ropiness in, 559  
   "sun-flavour" in, 564  
 Beetles, cigarette, control of, 443  
   flea, dusts for control of, 477  
   Khapra, life history of, 566  
 Beetroots, pectin from, 514  
   sugar, crops of, 507  
   viscous putrefaction of, 513  
 Beet sugar. *See under* Sugar  
 Bentonite in glazes, 276  
   packing of grapes in, 530  
 Benzanthrene, 218  
 Benzene, chlorination of, catalytic, 73  
   hexachloride, 72  
   effect of, on thermal stability of DDT, 441  
   insecticidal effect of, 438  
   sulphonation of, 73  
 $\delta$ -Benzene hexachloride, 442, 443  
 $\gamma$ -Benzene hexachloride, 442  
 Benzeneazonaaphthalenes, 81  
 3:4-Benzfluorene, 218  
 Benzydine-2 : 2'-diboronic acid, 81  
 Benzimidazoles as emulsion stabilisers, 638  
   1-substituted sulphonated, 76  
 Benzole absorption plants, corrosion and sludging in, 58  
 Benzoquinone, inhibition of polymerisation by, 349  
   reduction of, to hydroquinone, 73  
 Benzoxacarbocyanines, 641  
 Benzylpenicillic acid, 574, 609  
 DL-Benzylpenicillic acid, 575  
 Benzylpenicillin, 573, 604  
   biological precursors for, 574  
   determination of, 606  
 Benzylpenillic acids, 574, 575, 609  
 Bergaptene, 627  
 Beryllium in steel, 115  
   ores, concentration of, 128  
   vacuum melting and casting of, 133  
 Beverage plant, sanitation in, 565  
 Bezoars, 626  
 Bilharzia, chemotherapy of, 598  
 Biotin, 553  
 Bisdihydrodoisynolic acid, 595

3 : 4-Bis-(*m*-methyl-*p*-hydroxyphenyl)-  
2 : 4-hexadiene, 596  
*p*-Bis-(*p*'-nitrobenzeneazo)benzene, 81  
Bis(trimethylammonium) compounds with  
curare-like activity, 597  
Bitumens, viscosity of, 224  
Blastocholine, growth inhibition by, 472  
Bleach liquors, 314  
Bleaching, 314  
agents, optical, 76  
of pulp, 328  
Blood-plasma, dextran substitutes for,  
513  
Blue-print process, material for, 648  
Board, bagasse for production of, 510  
Boats, wood preservative for, 391  
Boiler plant, industrial, 202  
scale, removal of, 26  
water treatment, 24  
Boilers, corrosion of, 205  
deposits and slags from, 204  
smokeless, 208  
sugar, scale in, and its removal, 505,  
506  
use of secondary air in, 203  
with gas turbines, 203  
Boots, Army, deterioration of, 432  
Boric oxide in glass, 259  
Bornyl chloride, toxicity of, 443  
Boron deficiency in plants, 474  
in soils, 466  
determination of, in soils, 482  
Bottling plant, 562, 563  
Brass, stress-corrosion of, 144  
Bread, rye, 529  
staling of, 528  
wholemeal, 528  
Breakers, 50  
Brewery plant, microbiological control in,  
564  
Brewing, bacteriology of, 559  
proteins in, 563  
waters, correction of, 563  
Bricks, silica, production of, 276  
shortage of, 43  
Brine, cooling of, damage to concrete  
tanks for, 291  
Briquettes, magnesia, 180  
Briquetting, 200  
Bromine as disinfectant for swimming  
baths, 654  
number, determination of, 397  
Bromthymol blue in detergent analysis,  
252  
Bronzes, degassing of, 133  
Brucellosis, treatment of, 613  
Buffers for photographic fixing baths,  
644  
Bulls, nutrition of, for artificial insemina-  
tion, 484  
Burners, cyclone, 203  
Butadiene from alcohol and petroleum,  
218

Butadiene—*continued*  
heat transfer in boiling water mixtures  
of, 10  
polymers, latex from, 403  
Butane, catalytic dehydrogenation of,  
221  
*iso*Butane, boiling, heat transfer in, 10  
*iso*Butene, polymerisation of, 220  
But-1-en-3-one, 71  
Butter, aroma and flavour of, 526  
New Way process for, 525  
salted, storage of, 525  
Buttons from casein, 374  
*n*-Butyl alcohol, analysis of, mixed with  
toluene and water, 397  
Butyl titanate in paints, 392  
*N-iso*Butyl-2 : 6 : 8-decatrienoamide,  
442  
2 : 3-Butyleneglycol, production of, by  
fermentation, 565

## C

CR 39, mar resistance of, 347  
Caffeine, synthesis of, 585  
Calamus oil, "camphor" from, 626  
Calcium bisulphite in pulping, 326  
carbonate, froth flotation of, 177  
precipitated, production of, 177  
chlorate, basic, as weedkiller, 178  
cyanamide, 479  
hydride, production of, 183  
hypochlorite, production of, 171, 172  
lignin sulphonate, 327  
nitrate, production of, 165  
phosphate fluoride, 189  
production of, vacuum, 17  
Camazulene, 626  
Camphor, determination of, in cellulose  
nitrate, 374  
Cane sugar. *See under* Sugar  
Cannery wastes, disposal of, 663  
Canning, 534  
Carbazole dyes, 98  
Carbides in steel, 115  
Carbocyanines, 641  
Carbohydrates, books on, 516  
Carbon black from tar products, 229  
in rubber, 408  
combustion of, spectrum of, 201  
determination of, in soils, 482  
in steel, 118, 119  
dioxide, determination of, 560  
solid, production of, 182  
disulphide, production of, 170  
reactions of, with oxygen and steam,  
202  
Carbonisation, 39  
low-temperature, 39  
"Caronamide," 607  
Carrageen, polysaccharide from, 550

- Carrots, carotene in, 533  
 Caryophyllene oxide, 626  
 Casein, iodinated, effect of, on pigs, 486  
   plastics from, 374  
 Casks for beer, 563  
 Cassava starch, 492  
 Casting, semi-continuous, 132  
 Castor oil, dehydrated, 378  
   dehydration of, 379  
 Catalysts, activity of, and heat of  
   wetting, 225  
   adsorption, surface diffusion in, 13  
 Catalyst systems, Redox, 349, 406, 407  
 Cattle, composition of tissues of, 521  
 Cedarwood oil, 621, 624  
 Cedrene, determination of, 630  
 Cedrol, determination of, 630  
 "Ceepryn," 555  
 Cellophane, aluminium coating of, 17  
 Cells, electrochemical, primary, 159  
   secondary, 160  
 Cellulose acetate in packaging, 371  
   ripening of, 369  
   acid hydrolysis of, 310  
   adsorption of direct dyes on, 315  
   crystallinity of, 311  
   copper number test for, 312  
   derivatives, detergent properties of,  
     251  
     dyes for, 100, 101  
     esterification of, 369  
     extrusion of, 371  
     for plastics, 367  
     heat- and light-stabilisers for, 370  
   esters, anthraquinone dyes for, 97  
   esters and ethers, lacquers from, 394  
   etherification of, 369  
   ethers, 370  
   impregnation of, with synthetic poly-  
     mers, 319  
   nitrate, gelatinisation of, 374  
   pulp, acetylation of, 368  
   structure of, 309  
 $\alpha$ -Cellulose, determination of, in pulp,  
   333  
 Cement, acid-resisting, 29  
   aluminous, properties of, 290  
   analysis of, 289  
   Portland, chemistry of, 291  
   mixes for, 290  
   supersaturation of liquid phase of  
     pastes of, 177  
 Ceramic bodies, dry mixing of, 279  
   industry, nuclear physics applied to,  
     270  
 Ceramics, coating of, with metals, 279  
   colouring of, 280  
   firing of, 289  
   thermal shock resistance of, 279  
 Cereal products, determination of starch  
   in, 497  
   straw, Dutch, 324  
   for paper board, 322  
 Cereals, 527  
   growth and nutrition of, 466  
   vitamins in, 473, 553  
 Cerium, transformations in, 135  
 Charcoal, bone, heating of, in kilns, 9  
   in cane sugar refining, 506  
 Cheese, Camembert, ripening of, 525  
 Chemicals, finely-divided, dust elimina-  
   tion in handling of, 19  
   from petroleum, 217  
   inorganic, production of, 182  
 Chippers, 325  
 Chloral, manufacture of, 71  
 Chloramine as water disinfectant, 654  
 Chloranil, preparation of, 75  
 Chlorates, electrolytic production of, 173  
 Chlordano, insecticidal effect of, 438  
   toxicity of, 441  
 Chlorination in slime control, 331  
   photo-sensitised, 174  
 Chlorine as beer disinfectant, 554  
   dioxide as water disinfectant, 654  
   production of, 173  
   disinfection of water, 653  
   production of, 171  
 4-Chloro-2-amino-6-sulphonic acid, chro-  
   mium complex, 86  
 $\gamma$ -Chlorocrotylmecaptomethylpenicillin,  
   574  
 2-Chloroethylamine hydrochloride, pre-  
   paration of, 72  
 Chloromycetin, 566, 577, 613  
 2-Chloro-5-nitro-4-aminoacetoaceti-  
   nide, 75  
 Chloropierin, 479  
 Chlorosilanes, 363  
 Cholera, chemotherapy of, 598  
 Choline-esterase, depressor of, 435  
 Chromatography in sugar industry, 508  
 Chromium complexes with azo-dyes, 86  
   determination of, in chrome liquors,  
     431  
   electrodeposition of, 123  
   electrometallurgy of, 149  
   electroplating with, 150  
   oxide as Fischer-Tropsch catalyst  
     promoter, 221  
   plate for engine cylinders, 150  
   ores, concentration of, 128  
   resources, 103  
   sulphate solutions, conductimetric  
     titration of, 428  
 Chrysene, 218  
 Chua oil, 625  
 Cider waste waters, 663  
*Cinnamomum zeylanicum*, essential oil  
   from, 623  
 Cinnamon oil, 622  
 Citral, determination of, 629  
 Citrals, 627  
 Citrinin, structure of, 615  
 Citronella oil, 622, 623  
 Citroptene, 627

- Citrus fruits and oils therefrom, 621  
 juice and peel, determination of essential oils in, 631  
 oils, 623  
 -seed oils, 243  
 trees, fumigation of, 444
- Civetone, 628
- Cladosporium*, 331
- Clams, farming of, 523
- Classifiers, 24
- Clayden effect, 635
- Clay minerals, identification of, 288
- Clays, alumina from, 185  
 plasticity of, 275  
 water relationship to, 275
- Clayware, drying of, 279
- Clostridium*, growth of, in fish, 523
- Clostridium propionicum*, 559
- Clove oil, bactericidal action of, 626
- Coal, analysis of, 210  
 bituminous, carbonisation and gasification of, 48  
 dyes from, 101  
 briquetting of, 200  
 brown, stokers for firing with, 203  
 carbonisation of, 201  
   nitrogen oxides formed during, 54  
 chemical properties of, 197  
 classification of, 196  
 cleaning and drying of, 200  
 determination in. of sulphur, 210  
   of water, 210  
 dust explosions, 199  
 fauna and flora of, 197  
 gas. *See under* Gas  
 gasification of, high-pressure, 58  
   underground, 61  
 grinding of, 23  
 handling and storage of, 200  
 hydrogenation of, 199  
 mining and preparation, 199  
 oxidation of, 198  
 physical properties of, 197  
 price structure of, 62  
 pulverised, use of, 204  
 pyrolysis of, 198  
 sulphur in, 198
- Coal tar. *See under* Tar
- Coal washeries, 662
- Coalfields, Australia, 196  
 British Columbia, 196  
 Great Britain, 195  
 Poland, 196  
 Russia, 196  
 South Africa, 196
- Coatings, anti-corrosive, on steel, 389  
 protective, 123
- Cobalt-chromium alloys, 139  
 determination of, 381  
   in grass and hay, 482  
 electrometallurgy of, 130, 151  
 in glass, 268  
 transformations in, 135
- Coccidiosis, treatment of, 488, 489
- Coconut oil, hydrolysis of, 238
- Coffee processing, waste waters from, 664
- Coke, breakage of, 50  
 breeze, production of, 49  
   use of, 209, 210  
 calorific value of, 210  
 low-temperature, 201  
 manufacture of, 41  
 open-grate, quality of, 50  
 -oven practice, 41  
 -ovens, silica, life of, 43  
 properties of, 200  
 supply and shortages of, 42
- Colchicine, 583
- Cold-storage of fruit, 529  
 rooms for frozen foods, humidity of air in, 536
- Cold working and hydrogen embrittlement, 114
- Collagen, hide, analysis of, 430  
 structure of, 420
- Colonial Products Research Council, 515
- Colour formers, 646  
 photography, 645
- Columbium, production of, vacuum, 17
- Columns, fractionating, channelling in, 15  
 vapour-pressure bulb for control of, 28
- Composts, nitrogen inadequacy of, 463
- Compressors, centrifugal, 32
- Concentrators, sink-and-float, 127
- Concrete, durability of, 291
- Conophor oil, 378
- Contact time in reactions, 28
- Containers, canning, corrosion of, 535
- Control, "cascade" and "ratio," 28  
 instrumental, 28
- Copper, and its alloys, casting of, 132  
 arsenite, production of, 183  
 -chromium alloys, 139  
 corrosion of, as water pipes, 654  
 deficiency in swine causing anaemia, 539  
 determination of, in developers, 644  
 electroplating with, 151  
 etching of, by ferric chloride, 647  
 in soils, 455  
 metallurgy of, 130  
 ores, concentration of, 128  
 oxychloride, electrolytic production of, 183  
 pentachlorophenate for protection of insulating board, 335  
 powder, electrolytic production of, 152  
 -tin alloys, electro-deposition of, 155  
 tubes, thin, reversed torsion tests on, 141
- Corn, waxy, 495
- Corrosion, 120, 143  
 inhibitors, 122  
 of boilers, 26  
 of canning containers, 535

Corrosion—*continued*  
of water pipes, 654  
stress, 114  
Cotton, bleached, adsorption of Sky Blue  
FF by, 315  
bleaching of, 314  
dye for, 100  
linters, nitration of, 368  
purification of, 368  
vat-dyed, photochemical degradation  
of, 318  
Cottonseed, deterioration of, 235  
extraction of, 236  
meal, pigments in, and their removal,  
236  
oil, saturated glycerides from, 240  
Cottonwood trees, chlorosis in, 474  
Cracking, 221  
Crazing, 281  
Cream, 524  
*Crenothrix polyspora*, 332  
Crops, 464  
cereal, nitrogenous fertilisers for, 461  
farm, uptake of nutrients by, 461  
horticultural, plot tests with, 462  
hydraulic spraying of, 475  
Crotonic acid, 69  
*Cryptostegia grandiflora*, 403  
Crystal boundaries, 136  
Crystals, dislocation in, 142  
Curare, 584  
alkaloids, paralysing action of, 585  
Cuprous oxide, electrolytic production of,  
159, 183  
Cyanamide, production of, 166  
Cyanides, waste waters containing, 666  
Cyclamen aldehyde, 627  
Cymarin, 591  
Cymarol, 591  
*p*-Cymene, 627  
Cytase, activity of, 551

D

DDT, destruction of beneficial insects by,  
440, 441  
determination of, on agricultural pro-  
duce, 483  
dispersal of, as insecticide, 566  
penetration tests with, 438  
spraying of, 440  
toxicity of, to man and mammals, 441  
DDD, insecticidal effect of, 438  
*Dacrydium kirkii*, essential oil from, 624  
Dairy waste waters, treatment of, 663  
Damping-capacity, 140  
Date flour, 531  
Dates, 531  
De-enamelling of enamelled sheets, 283  
Degassing of metals, 133  
Dehydro- $\beta$ -ionone, 580  
11-Dehydropregesterone, 589

Density, measurement of, 267  
Dental caries, effect of fluorides on, 657  
Dentures, use of polymethyl methacry-  
late in, 346  
Deoxidation of steel, 111  
Depolymerisation, mechanism of, 349  
Desensitisation by optical sensitisers,  
640  
Desoxycorticosterone acetate, 589  
Desthiobenzylpenicillin, 574  
Desulphurisation, 222  
Detergency, 250  
in food industries, 537  
Detergents, 402  
additives to, 251  
analysis of, 252  
bottle-washing, 563  
from petroleum, 219  
synthetic, for wool scouring, 300  
waste waters containing, 665  
Deuterium oxide, production of, 182  
Deuterophenylacetyl-*N*<sup>15</sup>.DL-valine, 574  
Developers. *See under* Photographic  
Dextran, production of, 513  
Dextrinase, "limit," testing for, 551  
Dextrins from starch, 550  
De-zincing, vacuum, of lead, 131  
Diazo-compounds, decomposition of, 80  
Diazo-dyes, absorption spectra and  
structure of, 82  
Diazo process, 648  
Dibenzanthrone, catalytic amination of,  
99  
Dibenzyl ether linkages, determination  
of, 352  
3 : 5-Di-*tert*.-butyl-*p*-cresol, 73  
2 : 6-Dichloroanaphene, toxicity of, 443  
2 : 6-Dichlorocymene, toxicity of, 443  
Di-(2-chloroethyl)amine, treatment of  
chicks with, 490  
2 : 4-Dichlorophenoxyacetic acid for kil-  
ling bindweed, 472  
for pear-scald control, 530  
Die castings, zinc-base plating of, 155  
Dielectrics, 188  
"Diencestrol," 596  
Diethyl *p*-nitrophenylthiophosphate,  
toxicity of, 435  
1-Diethylaminopentan-4-ol, 72  
Di-2-ethylhexyl phthalate, evaporation  
of, 17  
Diffusion of gases through porous sur-  
faces, 12  
Difluoromalonic acid, 68  
Dihydro- $\gamma$ -ionone, 629  
Dihydrostreptomycin, 612  
Dihydroxyfluoroboric acid, production  
of, 183  
4 : 3'-Diketo-2'-phenyl-6-methyl-4 : 2' :  
3' : 4'-tetrahydropyrazolo-1' : 5'-1 :  
2-pyrimidine, 76  
Diluents, mineral, for insecticidal dusts,  
439

2 : 5-Dimethylhexan-3-one, 70  
 3 : 4-Dinitro-*o*-cresol, penetration of leaves by, 436  
 1 : 3-Dinitro-2 : 2-dimethylpropane, 397  
 2 : 4-Dinitrofluorobenzene, effect of, on wool, 299  
 1 : 2-Dinitro-2 : 4 : 4-trimethylpentane, 396  
 1 : 3-Dioxalane, polymer, in emulsions, 637  
 2-(3 : 4-Dioxyphenyl)tetrahydropyran, 436  
 Dipentene dihydrochloride, toxicity of, 443  
 Diphenylamine, preparation of, with ferric chloride as catalyst, 75  
 Diphenyls, diamino-, 74  
 Diphthaloylacidones, 99  
*Diplococcus glycinophilus*, 559  
*Diplophium africanum*, essential oil from, 622  
 Dips, fruit, to prolong storage life, 530  
 Disaccharides, fermentation of, 557  
 Disinfectants for beer, 554  
 Distillation, azeotropic, 13  
   data for, 14  
 Distillery wastes, disposal of, 663  
 Dodecylthiol as polymerisation accelerator, 407  
 Dogs, hysteria in, fed on "agenised" flour, 485  
 Dolomite, treatment of, 179  
 Dopes, metallic, anti-knock effect of, 225  
 Dough mixing, 529  
 Driers, cobalt, for linseed oil, 380  
 "Drikold," 56  
 Dryers, gas conveyor, 23  
 Drying, 22  
   freeze, apparatus for, 16  
 Duralumin billets, casting of, 132  
 Dusting with insecticides, 476  
 Dusts, agglomeration of, by ultrasonic waves, 20  
   combustible, dangers of, 19  
   determination of, 20  
   explosions of, 20  
   extraction plant for, from retort-house atmosphere, 51  
   removal of, from gases, 18  
   toxic, diluents for, 439  
 Dyeing, 314  
   fur felt hats, 301  
   glass fibres, 318  
   nylon, 304, 318  
   paper, 330  
   rayon viscose, 318  
   theory and practice in, 317  
   wool, 300  
 Dyes, acid, affinity of, for wool, 316  
   anthraquinone, 96  
   azo-, 80  
   contrast-lowering, 642  
   direct, adsorption isotherms for, 317

Dyes—*continued*  
   inhibition of yeast growth by, 556  
   pigment, 92  
   sensitising, action of, 640  
     new, 641  
   spectral absorption of, 640  
   transfer of, 647  
   vat, 97  
   water-soluble, 314

## E

E.605, 435  
 Earths, rare, in glass, 260  
 Eelworms, control of, 479  
 Eggs, dried, micro-organisms in, 527  
   liquid and frozen whole, pasteurisation of, 527  
   oiled, storage of, 526  
 Ejectors, steam jet, 18  
 Elastin, structure of, 421  
 Electrical analogor, 8  
 Electro-forming, applications of, 157  
 Electrolytic processes, 148  
 Electron microscopy in petroleum industry, 223  
 Electroplating baths for lead, 152  
   on aluminium, 149  
   on magnesium, 153  
   preparative treatment for, 157  
   shops, lay-out of, 158  
 Elemazulene, 626  
 Embrittlement, 114  
 Emicymarin, 591  
 Enamelling, 282  
 Enamels, 282  
   opacifiers for, 283  
   porcelain, as wallpaper, 285  
   preparation of, clay for, 282  
   removal of, 282  
*Enchytraeus albidus*, 661  
 Enniatins, 578  
   structure of, 616  
 Enzyme action, inhibition of, by methylbromide, 449  
 Enzymes, chemistry of, 551  
 Epsom salts, treatment of sole leather with, 433  
*Erysipelothrix rhusiopathiae* infection in turkeys, 489  
 Erythrosin, light absorption by, 640  
 Esterification, 239  
 Esters, 69  
 Ethers, 69  
 $\alpha$ -Ethoxyacrylic esters, 347  
 Ethoxysilanes, 363  
 Ethyl  $\alpha$ -acetamidooctoacetate, 585  
   alcohol from lactose, 558  
     from petroleum, 219  
   *See also* Alcohol  
 Ethylbenzene, catalytic dehydrogenation of, 220

Ethylene dibromide, nematocidal action of, 479  
 oxide, determination of, in wheat, 449  
 polymerisation of, 338  
 recovery of, from coke-oven gas, 57  
 tetrafluoride, 67  
 Ethylenediamine, production of, 71  
 Eucalyptus oil, 622, 624  
 Eugenol, bactericidal action of, 626  
 Eunoside, 591  
*Euonymus europaea*, glycoside from, 591  
*Euphorbia* resin, 403  
 Evaporation, 20  
 Evaporators, 20  
   heat transfer in tubes of, 21  
 Evodione, 627  
 Explosions, coal-dust, 199  
 Extraction processes, 12  
 Extractors, 12  
 Extrusion, 371

## F

Fabrics, permeability of, to air under pressure, 320  
   physical testing of, 319  
   resistance of, to water vapour, 319  
   vat-dyed, protection of, against photo-degradation, 318  
 Faeces, determination in, of starch, 496  
 Farnesol, 628  
 Fats, analysis of, 248  
   edible, 526  
   hydrolysis of, 238  
   interesterification of, 239  
   oxidative rancidity and flavour reversion of, 240  
   solvent extraction of, 237  
 Feeding-stuffs, 539  
   analysis of, 481  
   various, nutritive values of, for classes of stock, 487  
   protein values of, 486  
 Felspar, potassium, decomposition of, 175  
 Felt, paper-maker's, degradation of, 330  
   hats, fur, dyeing of, 301  
 Fenchenes, 628  
 Fermentation, industrial, 565  
   industries, 546  
   of disaccharides, 557  
   sequence of, 552  
 Ferrous sulphate, treatment of waste solutions of, 183  
 Fertilisers, American, magnesium status of, 460  
   analysis of, 480  
   application of, 461  
   in solution, 463  
   compound, granulation of, 458  
   nitrogenous, 164  
   nitro-phosphate, 460

## Fertilisers—continued

  phosphate, 167  
   production of, 458  
   sewage sludge as, 661  
 Fibre-board, pulp evaluation for, 334  
   waste liquors, 665  
 Fibres, animal, Young's modulus for, 307  
   organic, electron microscopy of, 296  
   plasticity of, 306  
   protein, 295  
     regenerated, 304  
     synthetic, 313  
   synthetic, 313  
     for filter cloths, 29  
     structure of, 295  
 Fillers for phenolic resins, 357  
   for polymers, 344  
 Filter cakes, fluid flow through, 6  
 Filters, for gases, 19  
   for molten sulphur, 168  
   rotary, setting of knife for peeling solids from, 28  
   sand, effect of air scour in, 653  
   sewage, 660  
 Finishing, 318  
   equipment, 319  
 Fins, heat transfer in, 8  
 Fire hazard in chemical plants, 32  
 Firebricks, production of, 285  
 Firing of ceramics, 289  
 Fish, effect of water toxicity on, 667  
   freezing of, 522  
   freshness of, 523  
   meal, determination of proteins in, 480  
   pastes, 522  
   preservatives for, 523  
   rancidity of, 523  
 Flax, retting of, 665  
 Flax plants, zinc deficiency in, 473  
   seed, detection of browning and wilt in, 468  
 Flies, house, resistance of, to insecticides 443  
 Flocculator, 652  
 Florite, water absorbent, 23  
 Flotation, froth, 127  
 Flour, "agenised," canine hysteria due to, 485  
   bleaching and enrichment of, 528  
   extraction rates in, 528  
 Fluid flow, 5  
 Fluidisation, mechanism of, 7  
 Fluoranthene, 218  
 Fluorides, removal of, from water, 657  
 Fluorine compounds in polymerisation reactions, 220  
   electrolytic production of, 158  
   preparation of, 170  
   removal of, from gases, 666  
 Fluoro-compounds, aliphatic, 67  
 Fluoroprene, 67  
 Flying-boats, anti-fouling paints for, 391, 406

- Fogs, insecticidal, 477  
 Folic acid, determination of, 537  
 Folic acid factor, 580  
 Food products, freeze drying of, 22  
     science, 520  
 Foods, analysis of, 537  
     canned, retention of vitamins in, 534  
     damage to, by fumigation, 448  
     dehydrated, hygiene of, 535  
     frozen, cooking of, 536  
         pre-cooked, microbiology of, 536  
         processed, 533  
         quality of, 539  
 Foot rot in cattle, treatment of, 488  
 Formaldehyde from methanol, 70  
     production of, 355  
     reaction of, with proteins, 305  
     solutions, distillation of, 14  
 Formocibazol, 598  
 Forticef for mouldings, 369  
 Foundry practice, 107  
 Fountain-pen caps, 158  
 Fractionation of petroleum and its derivatives, 219  
 Freeze drying, 22  
 Freezing of fruits and vegetables, 530  
 Fruit juices, 531  
     concentration of, 531, 532  
     syrops, ascorbic acid in, 536  
 Fruits, browning of, effect of ascorbic acid on, 531  
     cold-storage of, 529  
     dips and sprays for storage preservation of, 530  
     drying of, 535  
     freezing of, 530  
     pre-harvest drop in, growth substances for reducing, 472  
     setting of, 470  
     thinning of, growth substances for, 471, 472  
 Fuel, aviation, tests for, 225  
     coal and oil, flue gas losses with, 203  
     combustion of, in oxygen-enriched air, 11  
     economy, 208  
         in gas production, 46  
     gaseous synthetic, production of, 181  
     low-grade, use of, 209  
     oil, emulsions of, with sea water, 27  
     production and consumption of, 38  
     pulverised, firing with, 204  
         for gas turbines, 207  
     resources and production, 195  
     smokeless, 201  
     solid, analysis of, 210  
         domestic appliances for use with, 206  
         price structure of, 62  
         reactivity of, to oxygen, 202  
     utilisation, 202  
 Fumigants, 444  
     determination of, 449  
 Fumigants—*continued*  
     modes of application of, 444  
     soil, 445, 446, 479  
     sorption of, 447  
 Fumigation, 445, 478  
     of soils, 446  
     vacuum, 445  
 Fungi, growth of, in sewage, 661  
     stain from, on photographic negatives, 643  
 Fungicides, application of, 475  
     leather, 429  
 Furan solvents, 396  
 Furans, production of, 396  
 Furfuraldehyde, extraction of vegetable oils with, 237  
     in extraction, 11  
     resins from, 358  
 Furnaces, blast, design of, 106  
     effect of coke quality on operation of, 41  
     linings for, 205  
     scaffolds in, 106  
     use of oxygen in, 105, 205  
     industrial, 205  
     open-hearth, 109  
         use of oxygen in, 205  
     regenerative, 11  
     smokeless, 208  
     steel-making, 109  
  
 G  
 Gagetron, 28  
 Gallic acid, higher esters, antioxidant properties of, 242  
 Gas, coal, hydrogen sulphide removal from, 170  
     compressors, centrifugal, performance of, 7  
     combustible residual, removal of, from gas plant, 56  
     grid, South Yorkshire, 51  
     natural, drying of, 23  
     plants, German, 51  
     porosity of metals, 133  
     producer, 59  
     producers, Koppers, 59  
         thermal efficiency of, 60  
     production of, 46  
     purification, 52, 53  
     purifiers, insulation of, 52  
     retorts, heating of, by producers, 47  
     supply, South Wales, 51  
     tariffs, 48  
     town, 58  
     turbines. *See under Turbines*  
     water, 61  
     wood, 49  
 Gases, adsorption of, 12  
     cleaning of, 18

- Gases—*continued*  
 cracked, determination of olefins in, 226  
 determination of, in iron and steel, 119  
 diffusion of, through porous surfaces, 12  
 flow of, in pipes under reduced pressure, 17  
 industrial, 181  
 Gasification, 48, 58  
   underground, 61  
 Gasoline. *See* Petrol  
 Gasworks practice, 46  
 Gelatin for emulsions, 637  
   whale-skin, 637  
 Gelsemine, 584  
 Gems, synthetic, 277  
 "Gestogen," 589  
*Figartina stellata*, carrageen from, 550  
 Harimeter, 334  
 Glass, acidity and basicity of, 258  
   alkali-silicate, structure of, 257  
   analysis and testing of, 264  
   annealing of, 262  
   borax, magnetic susceptibility of, 268  
   borosilicate, heat-treatment and density of, 259  
   refractive index of, 263  
   chemical attack on, 268  
   coloured, 268  
   constitution of, 256  
   crystalline groupings in, 258  
   electrical properties of, 268  
   enamels, 268  
   eye-protective, 269  
   fibres, dyeing of, 318  
   strength of, 267  
   fracture of, 265  
   furnaces, 261  
   heat of formation of, 261  
   lead, stability of, 256  
   making, materials for, 259  
   mechanical properties of, 264  
   melting of, 260  
   furnaces for, 261  
   molten, attack on refractories by, 262  
   opal, structure of, 259  
   opaque, 269  
   optical, 270  
   annealing of, 263  
   phosphate, 259  
   photo-sensitive, 645  
 Pyrex, thermal expansion of, 259  
 rare earths in, 260  
 silicone films on, 271  
 stress-strain relationships in, 263  
 surface chemistry of, 270  
 surfaces, preparation of, for print glazing, 643  
 tank furnaces, 261  
 testing resistance of, to hydrofluoric acid, 264  
 viscosity-temperature relations of, 258  
 Glasshouses, fumigation in, 446  
 Glassware, breakage of, 266  
 Glazes, bentonite in, 276  
   crazing of, 281  
   lead, 280  
 Gliotoxin, structure of, 616  
 Gloss, measurement of, 334  
 Glucic acid, 514  
 Glucose, determination of, 561  
 Glutamic acid, synthesis of, 587  
 Glutathione, determination of, in yeast, 561  
   synthesis of, 588  
 Gluten, recovery of, from wheat, 494  
 "Glucose," 513  
 D-Glyceraldehyde-3-phosphate dehydrogenase, 553  
 Glycerides, analysis of, 248  
   trisaturated, formation of, 240  
 Glycerol, determination of, in fermentation residues, 561  
   production of, 218  
   by fermentation, 515  
 Glycine, preparation of, 72  
 Glyoxal from mineral oils, 218  
 Gold-platinum alloys, 139  
   salts for intensifying latent image, 636  
   solution of, in cyanide solutions, 131  
 Golden rod, 403  
 Grain, steeping of, for starch production, 493  
   stored damp, fungal damage to, 547  
 Grain size, 289  
 Gramicidin, 553, 577  
 Granular materials, heat transfer in, 9  
 Grape stems, alcohol from, 565  
 Grapefruit seed oil, 243  
 Graphite, chlorination of, 174  
 Grass, drying of, 50  
   effect of legumes on nutrition of, 465  
   fertiliser application to, 461  
   meal for fattening pigs, 486  
   pasture, determination of nitrogen in, 481  
 Gravel beds, granitic, heating of, 8  
 Greenfly, control of, 435  
 Grey speck in oats, 457, 467  
 Grinding, 23  
 Grisein, 614  
 "Grog," 285  
 Groundnut oil, hydrolysis of, 238  
 Growth substances, 470  
   determination of herbicidal effectiveness of, 483  
   fructigenic activities of, 471  
 S-Guaiazulene, 626  
 Gums in sugar factory, 513  
 Gutta-percha, crystallinity of, 405

## H

Halides, anhydrous liquid, purification of, 174

- Halogen organic compounds, fumigant, determination of, 449
- Hams, pork, curing, smoking, and pickling of, 521
- Hardeners for urea resins, 359
- Hardness, temporary, in boiler water, 25
- Hats, fur felt, dyeing of, 301
- Hay, digestibility of, 487
- Heart failure, treatment of, 592
- Heat-balances, 209  
of wetting, 225  
pumps, 207  
Norwich, 11  
regenerators, Frankl, 8  
transfer, 7  
-treatment, 115
- Heating, district, 206  
domestic, 206  
high-temperature, use of oxygen in, 202
- Heliopsis longipes*, active principle of, 442  
insecticide from roots of, 436
- Helleborus niger*, 591
- Hellebrin, 591
- Hemophilus para-influenzae*, growth factor for, 553
- $\alpha$ -Heptenal from soya bean oil, 526  
in flavour reversion, 243
- Herbs, flavouring value of, 539
- Herschel effect, 635
- Heterocyclic compounds, 76
- Hexachlorocyclohexane, synergist for, 437
- Hexadecahalogenophthalocyanines, 100
- Hexafluoroglutaric acid, 68
- Hexakisazo-dyes for leather, 87
- Hexamethylenediammonium adipate, polycondensation of, 361
- Hexamine, preparation of, 355
- n*-Hexane, boiling, heat transfer in, 10
- 1-(cycloHexen-1-yl)-3-methyl-1 : 3 : 5-octatriene-7-one, 579
- "Hexoestrol," 596, 597
- Hexokinase, yeast, 552
- Hexylresorcinol as coupling component for azo-dyes, 85
- Hide corium, constituents of, 422
- Hides, damage to, 422
- Homotryptophan, synthesis of, 587
- Hops, brewing trials with, 548  
varieties of, 547
- Horsechestnuts, starch from, 494
- Horticulture, fuel utilisation in, 207
- Houses, heating of, 206
- Humic acid, determination in, of carboxylic and phenolic groups, 211
- Humic acids, 199
- Humulon from hops, 548
- Hydrafiner, 329
- Hydrazine derivatives as sensitisers, 637
- 2-Hydrazinobenzthiazole, 637
- Hydrocaffeic acid, antioxidant properties of, 242
- Hydrocarbons, adsorption of, on silica gel, 13  
alkylation, polymerisation, and synthesis of, 219  
aromatic, and their derivatives, 72  
from petroleum, 218  
nitration of, 73  
chlorinated, 66  
combustion of, 49  
fluorinated, 67  
knock tendency of, 225  
mass spectrometry of, 224  
Raman spectra of, 224
- Hydrochloric acid, synthesis of, 172
- Hydrofluoric acid, recovery of, 171  
removal of, from gases, 666
- Hydrogen, absorption of, and cold work, 114  
as reducing agent for iron ores, 107  
chloride. *See* Hydrochloric acid  
cyanide, recovery of, 58  
determination of, in steel, 120  
fluoride. *See* Hydrofluoric acid  
in steel, and its removal, 112  
peroxide, preparation, properties, and uses of, 187  
- production and purification of, 182  
- pumps for, 18  
- sulphide, oxidation of, 170  
removal of, from gas, 52, 54
- Hydrogenation, 229, 237  
large-scale, catalyst support in, 206
- 3- $\beta$ -Hydroxyaetiobili-5-enic acid, 592
- Hydroxyanisole, butylated, antioxidant properties of, 242
- 3- $\beta$ -Hydroxybismorchol-5-enic acid, 592
- 17-( $\alpha$ )-Hydroxy-20-ketopregnanes, 590
- Hydroxylamine, preparation of, 166
- $\gamma$ -Hydroxyleucine, 586
- 8-Hydroxyquinoline, 580  
antiseptic action of, 555
- Hypo in developer-fixers, 644
- Hypochlorites, pulp bleaching with, 329
- I
- Ice, germicidal, 523
- Ice-colours, coupling compounds for, 75
- Impellers, multi-blade, flow pattern about, 6
- Indolylacetic acid as growth substance, 471
- Inks, printing, pigment dyes for, 92, 93
- Insect pests, 566
- Insects, resistant strains of, 443
- Insecticides, application of, 475  
application and distribution of, 439  
chlorinated-hydrocarbon, mode of action of, 442  
toxicity of, 439

**Insecticides—continued**

- contact, mode of action of, 442
- dust, diluents for, 439
- effect of light on, 437
- persistence of, under field conditions, 437
- phosphorus, 435
- phosphoryl ester, determination of, 435
- spraying of, from aircraft, 440
- vapour-phase, 444
- vegetable, 436
- Insemination, artificial, in dairy herds, 484
- Instrumentation in iron and steel works, 110
- Insulating board, testing of, 335
- Insulation, plastics for, 29
- Interesterification, 239
- Intermediates, 65
  - aliphatic, 66
  - aromatic, 72
- Iodides, determination of, in developers, 644
- Iodine value, determination of, 249
- Ion-exchange in boiler water treatment, 24, 25
  - in sugar industry, 515
- Iron alloys, degussing of, 112
  - and its alloys, heat-treatment of, 115
  - and steel industry, fuel consumption in, 209
  - bacteria, 332
  - cast, nodular structure in, 117
  - decarburisation of, in annealing, 115
  - determination of, in glass, 264
  - enamelling of, 275
  - grey, production of, 107
  - industry, oxygen in, 285
  - ore sinters, improvement of, 103
  - ores, treatment of, 104
  - oxide for hydrogen sulphide absorption, 182
    - spongy growth in, 288
  - pig-, production of, 105
  - solubility of, in beer, 564
  - whiteheart, peeling in castings of, 108
- Iron, 629
- Isocumulon, 548
- Isotopes, radioactive, as tracers in agriculture, 462

**J**

- Jams, ascorbic acid in, 536
- Jasmine oil, 622
- Jute, adsorption of methylene blue by, 312
  - as raw material for cellulose acetate, 367
- yellowing of, 314

**K**

- Kaolin, decomposition of, 277
- Keratin, 423
  - molecular structure of, 298
- wool, 296
- 1-Keto-2-methyl-7-methoxy-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-octahydrophenanthrene, 593
- Ketones, 70
- Ketoyohyrine, structure of, 584
- Kilns, British, firing of, 208
  - for magnesite, 179
  - light furniture for, 287
  - types of, 290
- Klerol, disinfectant action of, 654
- Krypton, production of, 182

**L**

- Lacquers, azo-dyes for, 92, 93
  - cellulose, testing of, 395
  - cellulose ester and ether, 394
  - nitrocellulose, 394
  - resins for, 386
- Lactic acid as meat preservative, 521
  - resins from, 385
- Lactobacillus casei* factor, 580
- Lactose, yeast fermentation of, 558
- Lakes, 92
- Laminating with polyesters, 361
- Lamps giving natural colour effects, 190
- Lateritins, 616
- Latex, rubber. *See* Rubber latex
  - synthetic, 402
    - creaming of, 403
- Lavender oil, 621, 624
- Lead chromes, 388
- Lead drosses, treatment of, 131
  - electroplating with, 152
  - electro-refining of, baths for, 152
  - in glazes, 280
  - salicylate as pigment, 389
  - titanate as pigment, 388
  - zinc ores, treatment of, 128
- Leaf-hoppers, sugar-cane, 512
- Leaks, detection of, 16
- Leather, ageing tests on, 432
  - analysis and testing of, 430
  - azo-dyes for, 87
  - boot and shoe, deterioration and water penetration of, 431, 432
  - chrome-calf, 432
  - chrome-tanning of, 429
  - industry, fungicides for, 429
  - sole, synthetic tan for, 427
    - treatment of, after tanning, 433
  - substitute, nylon as, 363
  - water penetration of, 431
- Leaves, protein of, 537
- Lecithin in flavour reversion, 243

- Leclanché* cells, 159  
*Lecytophora lignicola*, 331  
 Legumes, effect of, on nutrition of grasses, 465  
 Lemongrass oil, 622  
*Leptospira canicola* infection, treatment of, 489  
 Lethane, resistance of flies to, 443  
 Leucaenine, 587  
 Licheniformin, 578  
 Lignin sulphonates, 327, 426  
 Lime, "soft" burnt, "fluo-solids" process for, 177  
     kilns, 176  
 Lime seed oil, 243  
 Limestone, neutralisation of waste acids with, 177  
     quarrying of, 176  
 Linaloe oil, 624  
 Linoleic acid, determination of, 248, 526  
*iso*Linoleic acid in flavour reversion, 242  
 Linolenic acid, determination of, 381  
 Linseed, cultivation of, 467  
     weed control for, 468  
     oil, 377  
         autoxidation of, in presence of metal soaps, 381  
         drying of, 380  
         flavour reversion in, 242  
         heat-polymerised, fractionation of, 247  
         hydrogenation of, 237  
         solvent extraction of, 12  
         stand oil, polymers in, 380  
 Lipase, microbial, 525  
 Lipides, synthesis of, 526  
 Lipoxidase, 526  
*Lippia asperifolia*, essential oil from, 624  
 "Liquidusters," 477  
 Lithium, determination of, in soils, 482  
     compounds in enamels, 284  
     -magnesium alloys, transformations in, 135  
         manganite, 284  
         production of, vacuum, 17  
         titanate, 284  
         transformations in, 135  
         zirconate, 284  
 Lithography, 648  
 Lithopone, barytes used for, 178  
 Liver, nutritive value of, 521  
 Locomotives, 207  
 Lubricants for yarn spinning, 301  
     hydrocarbon, synthesis of, 227  
 Lubricating oils, additives for, 220  
     engine-testing of, 227  
     synthesis of, 228  
 Lubrication, 227  
 Lucerne, drying of, 535  
     growth of, in manganese deficiency, 457  
     growth and fertilisation of, 466  
*Lumbricillus lineatus*, 661  
 Luminescents, 188  
 Lupulon from hops, 548  
 Lycomarasinin, 553  
*Lymphogranuloma venereum*, treatment of, 613

## M

- Macromolecular substances, swelling of, 405  
 Magnesite, dead-burning of, 179  
 Magnesium alloys, corrosion protection of, 143  
     -base alloys, corrosion of, 143, 144  
     carbonates, 180  
     chloride, anhydrous, 180  
     deficiency in plants, 474  
     electrolytic production of, 153  
     electroplating on, 153  
     oxide, crystal growth of, 179  
         material for reduction, 179, 180  
         production of, 179  
     oxychloride for cement, 180  
     production of, 129  
         vacuum, 17  
 Maize starch, 493  
 Maleic anhydride, addition products of, 241  
 Malt,  $\alpha$ - and  $\beta$ -amylase activity of, 551  
     analysis of, 560  
 Malting, 549  
 Maltose syrups, preparation of, from flour, 550  
 Manganese, deficiency of, in relation to crops, 457  
     in soils, 463  
     in soils for oats, 467  
     dioxide, production and uses of, 183  
     electrometallurgy of, 152  
     in soils, 456  
         in relation to copper, 456  
     ores, treatment of, 129  
     removal of, from water, 657  
     resources, 103  
 Mannosidostreptomycin, 575  
 Manures, green, 463  
 Margarine, 526  
     fortification of, with vitamins, 538  
 Mass transfer, 11  
 Mastitis, control of, 488, 489  
 Mayonnaise, 537  
 Meat and meat products, 520  
     canning of, 535  
     dried, vitamins in, 535  
     frozen, 522  
     nutritive value of, 521  
     pastes, 522  
     quality tests for, 521  
 Medicinals, 573  
 Medicines, veterinary, 488  
*Melaleuca*, essential oils from, 620  
 Melamine, preparation of, 360

- Melamine-formaldehyde polymers, 332  
 Melanoidins, 564  
*Melia azadirachta*, essential oil from, 624  
 Meningitis, tubercular, treatment of, 610  
 Menthofuran, 628  
 DL-Menthol, production of, 629  
 Mepacrine in veterinary practice, 489  
 Mercaptobenzthiazole as anti-foggant, 638  
 Mercapto-1 : 3 : 4-thiadiazole in emulsions, 639  
 2-Mercapto-4 : 6 : 6-trimethylthiazine, wetting agent from, 402  
 Mercurials in slime control, 332  
 Mercury as fumigant, 446  
 Metabolism cage for animals, 535  
 Metal cleaners, 252  
   surfaces, cleaning of, for painting, 56  
 Metaldehyde, 70  
 Metallisation of azo-dyes, 85  
 Metallography, 134  
 Metallurgy, high vacua in, 17  
 Metals, cleaning of, 157  
   electro-polishing of, 156  
   internal stresses in, 113  
   lubrication of, 227  
   non-ferrous, 127  
   plastic flow in, 140  
   pure, transformations in, 135  
   recrystallisation in, 135  
   spraying of, on to ceramic surfaces, 279  
   trace, combination of, with antiseptics, 555  
   under stress, 140  
 Methacrylic acid, preparation of, 344  
   esters, 346  
 Methacrylonitrile, synthesis of, 347  
 Methane, conversion of, to acetylene, 11  
 Methionine, synthesis of, 587  
 Methyl bromide as fumigant, 446, 447  
   determination of, 449, 450  
   reactions of with food constituents, 449  
   toxicity of, 445  
   ethyl ketone, 70  
    $\alpha$ -fluoroacrylate, polymerisation of, 344  
   linoleate, autoxidation of, 241  
   methacrylate, polymerisation of, 345  
   oleate hydroperoxide, 526  
   maleic anhydride addition product of, 241  
   isopropenyl ketone, polymerisation of, 348  
 3-Methyl-4-carbethoxycyclohex-2-ene-1-one, 592  
 3-Methylcitral, 626  
*cis*-9-Methyl-1-decalone, 594  
 3-Methyl-4 : 6-di-*tert*.-butylcyclohexanol, 373  
 1-Methyl-4-(diethylaminoethylamino)-xanthone, 598  
 3-Methyl-7 : 8-dihydrolinalool, 626  
 $\alpha$ -Methyl- $\alpha$ - $\beta$ -di-(*p*-hydroxyphenyl)valeric acid, 596  
 Methylene blue, absorption of, by vegetable fibres, 312  
   in detergent analysis, 252  
 Methylenequinones, formation of, in vulcanisation, 355  
 1-Methyl-1'-ethyl-2 : 2'-cyanine chloride, 640  
 3-Methylgeraniol, 626  
 Methylionones, 626  
*cis*-1- and -2-Methyl-7-methoxyhexahydronaphthalene-1 : 2-dicarboxylic acid anhydrides, 593  
 Methylol group, determination of, 352  
 $\alpha$ -Methylstyrene, 340  
 Mica, distinction between pyrophyllite, talc, and, 440  
*Micromeria rotundifolia*, essential oil from, 624  
 Micro-organisms, effect of, on corrosion, 143  
   in raw sugar, 513  
 Milk and milk products, 524  
   dried skim, deterioration of, in storage, 524  
   handling, production, and testing of, 524  
 Mills for determination of heating properties, 333  
   revolving disc, 325  
 Mimosa tannin, 425  
 Mineral resources, 103  
 Minerals as diluents for insecticidal dusts, 439  
   dressing of, 127  
   froth flotation of, 127  
 Miner's lamps, cells for, 160  
 Miracil D, 598  
 Mirrors, metallic, 158  
 Mites, control of, 443  
 Mixers, 21  
 Molasses, uses of, 509  
 Molybdenum alloys, electro-deposition of, 156  
   deficiency in soils for oats, 467  
   resources, 103  
 Montan wax. *See under* Waxes  
 Moth borers, sugar-cane, 512  
 Moths, codling, control of, 440  
 Moulding articles from polyvinyl pastes, 343  
   injection, 370  
   powders, production of, 370  
 Mouldings, amino-plastic, testing of, 359  
   phenolic, microscopy of, 356  
 Moulds, grain damage by, 547  
   riboflavin production by, 554  
 Mulching materials, 455  
 Mullite, formation of, 277  
 Musarin, 614  
 Muscle, biochemistry and physiology of, 520  
   fatigue in, 521

Muscone, 626  
DL-Muscone, 623  
Mycelianamide, structure of, 616  
Mycophenolic acid, structure of, 616  
*Myzus persicae*, control of, 436

## N

Naphtha, desulphurisation and reforming of, 222  
2-Naphthoxyacetic acid as growth substance, 470  
Naphthylacetic acid as growth substance, 471  
*Narcissus poeticus*, essential oil from, 624  
Neats foot oil, 244  
Nematocides, 479  
Neobietic acid, 383  
Neocyanines, 641  
Neriifolin, 592  
Neroli oil, detection of adulteration in, 630  
Nerolidol, 628  
Nickel, electro-deposited, properties of, 153  
    electrodeposition of, 123  
    electrometallurgy of, 153  
    electroplating with, 154  
    electropolishing of, 156  
    -silver castings, gas-unsoundness of, 134  
    subsulphide as catalyst in gas purification, 55  
Nicotine as insecticide, 436  
Nicotinic acid, determination of, 537  
    in barley and yeast, 554  
Nitric acid, production of, 165  
    pure, transport of, 30  
Nitro-alcohols, 68  
Nitro-2-alkoxyanilines, as sweetening agents, 74  
*m*-Nitroaniline, electrolytic reduction of, 74  
Nitrocellulose, structure of, 312  
Nitro-compounds, 396  
    aromatic, reduction of, 74  
Nitro-dyes, 100  
Nitrogen, combination of, with oxygen, in regenerative furnace, 11  
    compounds, assimilation of, 557  
    determination of, 561  
    in organic materials, 430  
    organic compounds, reactions of methyl bromide with, 449  
    oxides, production of, 165  
    removal of, from steel, 112  
    trichloride, preparation of, 166  
"Nitrogen-mustards" in veterinary practice, 490  
Nitro-hydrocarbons, 68  
Nitro- $\alpha$ - and - $\beta$ -naphthylamines, 74

Nitro-olefins, 397  
Nitro-phosphate, 460  
Nitrous oxide, liquid, freezing foods with, 536  
Norconidendrin, antioxidant properties of, 242  
Nutrition, animal, 484  
Nylon, azo-dyes for, 89, 91, 92  
    dyeing of, 304, 316, 318  
    mol. wt. of, 314  
    production of, from cyclohexane, 218  
    structure and properties of, 302  
    use of, for coatings, 385  
    uses of, 363

## O

Oats, grey speck in, 457, 467  
    mildew on, 467  
    trace element deficiencies in, 467  
*Ocimum*, essential oils from, 625  
Octamethylene- $\alpha$  :  $\omega$ -bistrimethylammonium chloride, 597  
Oestrogens, 591  
    synthetic, 596  
Oestrone, isomer of, 593  
    synthesis of, 593  
Oil refinery waste waters, 606  
    seeds, 235  
    shale deposits, 228  
    recovery of oil from 40  
Oils, analysis of, 248  
    anthraquinone dyes for, 99  
    drying, 247, 377  
    analysis of, 381  
    polymerisation of, 380  
    essential, analysis of, 629  
    sources of, 620  
    fatty, hydrogenation of, 237  
    interesterification of, 239  
    solvent extraction of, 237  
    fuel, emulsions of, with sea water, 2  
    lubricating. *See* Lubricating oils  
    mineral, 216  
    analysis and testing of, 223  
    desulphurisation of, 222  
    refining of, 221  
    vegetable, furfural extraction of, 12  
    stability of, 241  
Olefins, analysis of, 397  
    determination of, in cracked gases, 226  
Onion juice, 532  
    oil, 623  
    seed, sorption of methyl bromide by, 447  
Opacity in glass, 269  
Optical sensitisation, 639  
Orange juice, 532  
    ascorbic acid in, 473  
    drying of, 16, 22  
    seed oil, 243  
Otto of rose, standards for, 630

- Oxides as colouring additions to glass, 269  
 glass-forming, 256  
 hardening of, in gas purifiers, 52  
 phase diagrams of systems of, 258  
 refractory, sintering of, 278
- Oxycelluloses, determination of carboxyl group in, 311
- Oxygen, combination of, with nitrogen, in regenerative furnace, 11  
 determination of absorption of, 658  
 determination of, in beer and worts, 560  
   in steel, 119, 120  
 dissolved, removal of, from boiler feed water, 656  
 in blast furnaces, 105, 107  
 in iron and steel industry, 285  
 in town gas manufacture, 59  
 production of, 30  
 production and uses of, 181  
 use of, in high-temperature heating, 202  
   in iron and steel industry, 205  
   in steel-making, 110
- Oysters, effect of sulphate pulp wastes on, 653
- Ozone, production of, 182  
 solubility of, in water, 654

## P

- "PASA," 588
- Packing materials, plastic, 371
- Paesia scaberula*, essential oil from, 625
- Paint industry, high vacua in, 16  
 primers for corrosion protection, 143
- Paints, 387  
 anti-corrosive, 389, 390  
 anti-fouling, for flying-boats, 391  
 cementiferous, as primers for anti-fouling pigments, 123  
 decorative, 390  
 exposure tests for, 390  
 fire-resistant, tests for, 392  
 rubber compounds in, 406  
 ships', 391  
 silicone resins in, 385  
 under-water anti-corrosive, tests for, 391  
 white, house, 390  
 zinc oxychloride, 392
- Palm oil, saturated glycerides from, 240
- Pantothenic acid in brewing, 554
- Paper board, corrugating, production of, 323  
 coating of, 331  
 dyeing of, 330  
 fibre orientation in, 330  
 glassine, 314  
 industry, starch in 496  
 machines, 330

## Paper—continued

- making, 329  
 bamboo for, 324  
 melamine-resins for increasing wet strength of, 360  
 metal coating of, vacuum, 17  
 mills, slime control in, 331  
   waste waters from, 665  
 production, 322  
 production and properties of, 314  
 pulp, bleached, 323  
 raw materials for, 322  
 strength of, effect of starches on, 501  
 testing of, 334  
 wet-strength, 332
- Paraffins, dehydrogenation and cyclisation of, 220
- iso*Paraffins, alkylation of, with olefins, 219
- "Parathion," 435
- Parthenocarp in fruits, 471
- Particle size in finely-ground powders, 24  
 measurement of, 289
- Particles, behaviour of, under stress, 23  
 nuclear, recording of, with photographic emulsions, 636  
 track plates for, 643
- Passivity, 122
- Peaches, packing and storage of, 530
- Peas, hardness of, after cooking, 533
- Peat, properties, winning, and uses of, 197
- Pectin, preparation and uses of, 536  
 production of, 514
- Penicillic acid, synthesis of, 616
- Penicillin, 573, 603  
 assay of, 606  
 bacteriostatic action of, 607  
 chemistry of, 608  
 crystalline salts of, 606  
 drying of, 16  
 in veterinary practice, 489  
 isolation and purification of, 605  
 legislation about, 603  
 production of, 603  
 treatment with, 607
- Peppermint oils, 621, 624
- Peppers, sweet, canning of, 535  
 drying of, 536
- Peptides, absorption of water by, 313
- Perfumes, fixation of, 623
- Perilla oil, hydrogenated, flavour revision in, 242
- Periplocymarin, 591
- Periplogenin, 590
- Peroxidases, 551
- Pests, insect, 566  
   on sugar-cane, 512  
   non-insect, chemical control of, 443
- Petitgrain oil, detection of adulteration in, 630
- Petrol, cracked, hydrocarbon-type analysis of, 226

- Petrol**—*continued*  
 from Middle East crude, 229  
 sulphur compounds in, 222
- Petroleum**, analysis and testing of, 223  
 bibliography of, 230  
 chemicals from, 217  
 fogs from, 477  
 industry in war, 228  
 pipe stills for, 56  
 products, distillation of, 14  
   for rubber industry, 409  
 refinery waste waters, 666  
 refining of, 51, 221  
 reviews and surveys of, 228  
 wax. *See under* Waxes  
 world demand for, 229
- Pharmaceuticals**, calcium carbonate in, 178
- Phenanthridium** compounds in veterinary practice, 490
- Phenol**, antiseptic action of, 555  
 production of, from benzene, 73, 355  
 recovery of, from weak aqueous solutions, 13
- Phenols**, 73  
 alkylation of, 73  
 production of, 355
- $\alpha$ -Phenyl-(3 : 4-dioxymethylene)acrylonitrile, 436
- o*-Phenylenediamine oxidase, 551
- 1-Phenylethanol, preparation of, 75
- Phenylmercuric lactate, toxicity of, to fish, 667
- Phenylpantothenone, antagonism of, to pantothenic acid, 554
- Phosphate rock, mixing sulphuric acid with, 22
- Phosphates**, 166  
 in supplementary feeds for chicks, 485
- Phosphoric acid**, production of, 167
- Phosphors**, 188  
 barium, 178
- Phosphorus**, production of, 167  
 red, oxidation of, 167  
 production of, 167
- Photographic developers**, 642  
 analysis of, 644  
 colour, 645  
 development, 642  
 emulsions, 636  
   silver bromide, ripening and sensitivity of, 637  
 film bases, 642  
 films, "contour," 645  
   effect of supersonic vibrations on, 636  
   high-speed processing of, 643  
 fixing-baths, 644  
 latent image, formation of, 633  
 negatives, colour masking in, 646  
 papers, bronzing of, 638  
 plates, warm-tone lantern, 644  
 processes, blue-print and diazo, 648  
 processing, 642
- Photographic**—*continued*  
 reversal process, 644  
 sensitisation, 639  
 sensitivity, theory of, 633  
 stains, removal and prevention of, 643  
 supersensitisation, 641
- Photography**, colour, 645  
 colour formers for, 76
- Photogravure** printing plates, 648
- Photo-lithography**, albumin solution for, 648
- Photo-mechanical** processes, 647
- Phragmites communis*, pulp from, 324
- Phthalic acid**, preparation of, 75
- Phthalocyanines**, 99
- Phyllocladus trichomanoides*, essential oil from, 625
- Phytin** in brewing materials, 564
- Phytomonas betae-gelatae*, 513
- Pickles**, curing of vegetables for, 533
- Pigments**, 92, 387  
 aluminium paste, 389  
 calcium carbonate for, 178  
 lead, 387, 388  
 lemon chrome, 388  
 titanium, 387, 390
- Pigs**, fattening, nutrition of, 486
- iso*Pimpinellin, 627
- Pine oils**, 622  
 Huon, 621
- Pineapple juice**, sugar recovery from, 515
- Piperazine**, preparation of, 76
- Piperonyl butoxide** as pyrethrum synergist, 436
- Pitch**, briquetting of, 56  
 coal-tar, constituents of, 56
- Pivalic acid**, amino-, 72
- Plant**, American, wartime development of, 16  
 design and control of, 27
- Plants**, copper in nutrition of, 455  
 damage to, by insecticides, 441  
 hormones, 470  
 manganese in nutrition of, 456  
 mineral deficiencies in, 473  
 nematodes, control of, 479  
 roots, absorption by, 454  
 tissues, penetration of, by fungicides and insecticides, 438  
 vitamins in, 472
- Plaster**, swelling of, 291
- Plasticisation**, 370
- Plasticisers**, 343  
 for cellulose derivatives, 372, 394  
 monomeric and polymeric, 373  
 sulphonamide, 374  
 theories of action of, 373
- Plasticity**, 275  
 of fibres, 306
- Plastics**, cellulose acetate, properties of, 372  
 cellulose derivative, 367  
 production and uses of, 370

- Plastics—continued**  
 coating of pipes with, 29  
 dielectric and optical properties of, 372  
 in packaging, 371  
 in the textile industry, 319  
 industry, high vacua in, 16  
 metallisation of, 16, 158  
 phenolic, 352  
 processing of, 356  
 protein, 374  
**Plastimeters** for rubber, 405  
**Platinum** catalysts for sulphur dioxide  
 oxidation, 169  
 wire, heat transfer from, to water, 10  
**Plot tests** for horticultural crops, 462  
**Plums**, Victoria, cold-storage of, 529  
**Pneumonia**, treatment of, 613  
**Polishing**, electrolytic, of metals, 156  
**Polyamides**, 361, 385  
 foam inhibition by, 10  
 mol. wt. of, 362  
**Polycondensation** products, 352  
**Polyesters**, formation of, 360  
**Polyethylene**, 338  
 terephthalate, 361  
**Polyglutamic acid**, 295  
**Polymer** films, water-vapour permea-  
 bility of, 319  
**Polymerisation**, 220  
 accelerators, 407  
 emulsion, kinetics of, 348  
 inhibitors, 349  
 of drying oils, 380  
 of vegetable oils, 247  
**Polymers**, acrylic, 344  
 cross-linking, 347  
 fluorine-containing, 344  
**Polymethyl methacrylate**, degradation  
 of, 349  
 stress cracking of, 346  
**Polymixins**, 576, 615  
**Polyoxyethylene stearate**, effect of, on  
 bread, 529  
**Polypeptides**, synthetic, 295  
**Polystyrene**, 339  
 pyrolysis of, high vacuum, 349  
**Polytetrafluoroethylene**, pyrolysis of, 344  
**Polythene**, 338  
 production and uses of, 220  
**Polyvinyl chloride**, 342  
 plasticising of, 343  
 paste technology, 343  
**Poplar wood**, pulp from, 368  
**Poppyseed**, 468  
**Poppyseed oil**, solvent extraction of, 237  
**Porcelain**, enamelling of, 282  
 for electrical industry, 278  
 industry, ceramics for, 274  
 semi-conducting, 280  
**Pork**, cooking, curing, and storage of, 534  
**Potash alunite** as fertiliser, 460  
 determination of, in fertilisers, 461,  
 481  
**Potassium chlorate**, production of, 173  
 determination of, in soils, 482  
 hydroxide suspensions, 176  
 perchlorate, production of, 173  
**Potato starch**, 493  
**Potatoes**, solanine in, 533  
 sorption of methyl bromide by, 447  
**Pottery** industry, 274  
**Poultry**, vitamin requirements of, 484  
**Precipitators**, electrostatic, 18  
**Pre-collagen**, 422  
**Pregnane** derivatives, 589  
**Pregn-20-enes**, 590  
**Preservatives**, fish, 523  
**Preserves**, acetic acid, 537  
**Pressure** drop through granular material,  
 6  
 vessels, 27  
**Printing** images on plastic base, 648  
**Procaine** penicillin, 573  
**Producers**, mechanical, 47  
**14-*allo*-17-*iso*Progesterone**, synthesis of,  
 589  
*iso*Propylphenyl *isopropyl* ether, 73  
**Protein** fibres, 295, 304, 313  
**Proteins** as emulsion retarders, 638  
 hide, 422, 423  
 introduction of sulphur into, 305  
 plastics from, 374  
 reaction of, with formaldehyde, 305  
 structure of, 295  
**Prunes**, drying of, 536  
**Psittacosis**, treatment of, 613  
**Pteric acid**, 553, 580  
**Pteric-glutamic acid**, 553  
**Pteroylglutamic acid**, 580  
**Pteroylheptaglutamic acid**, 580  
**Pteroylhexaglutamylglutamic acid**, 580  
**Pteroyltriglutamic acid**, 580  
**Pulp**, bamboo, 324  
 beating of, 329  
 bleaching of, 328  
 evaluation of, for fibreboard, 334  
 production of, 324  
 sizing of, 330  
 testing, 333  
**Pulping**, alkaline, 325  
 bisulphite processes, 326  
 neutral sulphite processes, 328  
**Pulveriser**, 204  
**Pumping**, speed of, in micron range, 15  
**Pumps**, 6, 7  
 heat-, 207  
 vacuum, 18  
**Purging** machine for gas plant, 56  
**Putrescine**, 553  
*Pycnanthemum pilosum*, 621  
**Pyelonephritis**, bovine, treatment of, 489  
**Pyrazolone** dyes, 83  
**Pyrene**, 218  
**Pyrethrins**, mode of action of, 442  
**Pyrethrum**, and its synergists, 436  
**Pyridoxal**, 553

Pyridoxamine phosphate, 553  
 Pyridoxine in beer, 534  
 Pyrogallol oxidase, 551  
 Pyrometry in ceramic industry, 271  
 Pyrophyllite, distinction between mica, tale, and, 440

## Q

*iso*Quinoline red chloride, 640  
 Quinone. *See* Benzoquinone  
 Quinones, chlorinated, 75

## R

Rabbit burrows, fumigation of, 444  
 Radiography, opaque agents for, 82  
 Rancidity, oxidative, 240  
 Rayon, cellulose acetate, azo-dyes for, 87  
   cord for tyres, 403  
   dyeing, printing, and finishing of, German, 318  
   viscose, brown pigments for, 93  
   dyeing of, 318  
 Rays, cathode, tubes, luminescent screens for, 189  
 Recrystallisation in alloys and metals, 135  
 Redox catalyst systems, 349, 406, 407  
   potential of developers, 643  
 Reduction, physical chemistry of, 129  
 Reductone, reaction of, with *p*-amino-benzoylglutamic acid, 581  
 Refiners for paper pulp, 330  
 Reflectometer, 268  
 Refractories, attack of, by molten glass, 262  
   basic, for steel furnaces, 288  
   bonding agents for, 286  
   carbon, for blast furnaces, 106  
   for iron and steel furnaces, 285  
   glass tank, 262  
   production of, 285  
   sintered, 274  
   oxide, 286  
   slagging and service life of, 288  
 Refrigeration plant, 32  
 Regenerators, 208  
 Resiliency, definition of, 307  
 Resins, alkyl, 383  
   ethenoid silicon-containing, 384  
   for cellulose lacquers, 394  
   fossil, 383  
   furan, 358  
   ion-exchange, 25, 357  
     in analysis, 431  
     in fruit-juice treatment, 531  
   melamine-formaldehyde, 332, 333, 359  
   natural, 383  
   phenol-formaldehyde, 383

Resins—*continued*

  phenolic, 352, 383  
     applications of, 357  
     fillers and modifiers for, 356  
     for bonding of rubber to textiles, 415  
     hardened, structure of, 353, 354  
     processing of, 356  
     testing of, 356  
   silicone, 363, 385  
     for fire-resistant paints, 392  
   synthetic, 382  
   thiophen, 358  
   urea, production and processing of, 359  
   urea-formaldehyde, 332, 358, 384  
 Resistors, silicon carbide, for furnace heating, 290  
 Resols, production of, 355  
 Retarders for emulsions, 638  
 Rhamnose, structure of, 590  
 Rhizopterin, 581, 582  
 Rhodium, electroplating with, 154  
 Riboflavin in Brazilian vegetables, 537  
   production of, by fungi, 537  
     by moulds, 554  
*n*-Ribitylaniline, 74  
*n*-Ribityl-*o*-4-xylydine, 74  
 Rice, milling of, 529  
 Rockets, propulsion of, 5  
   hydrogen peroxide for, 187  
 Rocks, for silica brick production, 276  
 Rope in beer, 559  
 Rosin as modifier for phenolic resins, 356  
   sizing, 330  
 Rotenone, synergists for, 436  
 Roughness tester, 334  
 Rubber, ageing of, 412  
   bonding of, to metal, etc., 414  
   chlorinated, 406  
   compounding materials for, 408  
   consumption and output of, 399  
   derivatives, 406  
   guayule, 403  
   hydrocarbon from latex, 406  
   latex, 399  
     coagulation of, 401  
     compounding of, 402  
     creaming agents for, 400  
     *Herea*, stability of, 400  
     preservatives for, 400  
     purification and concentration of, 401  
   properties of, 404  
   raw, sources of, 403  
   reclaiming of, 413  
   soles, synthetic, 407  
   swollen, properties of, 412  
   synthetic, "cold," 407  
     fluorine-containing, 408  
     GR-S, 402, 406  
     softeners for, 409  
   Lactoprene, 408  
   reclaiming of, 413  
   silicone, 408

- Rubber—*continued*  
 tyres, bonding of nylon or radon for, 414  
 "cold rubber," 407  
 use of rayon cord for, 403  
 uses of, 29  
 vulcanisation of, 355, 409  
 vulcanised, 410  
 Rubber-seed oil, 378  
 Rum from molasses, 509  
 Rutile, production of, 186  
 "Ryanex," use of, against sugar cane borer, 436  
*Ryania speciosa*, 436  
 Rye bread, 529
- Saccharification, 502  
 Safranine as developer accelerator, 644  
 Safrole, determination of, 630  
 Sage oil, 625  
 Sago flour, supply of, 492  
 "Saleomine," 31  
*Salmonella* in dried egg, 527  
 Salt cake, manufacture of, 175  
 Sarcolemina, structure of, 421  
 Sarmentocynarin, 591  
 Sarmentogenin, 591  
 Sausages, soya, 522  
 Scale formation in sugar plant, 505  
 removers for, 506  
*Schistosoma japonicum*, 661  
 Scouring of wool, 300  
 Sea water. *See under* Water  
 Seal oil, Atlantic grey, constituents of, 247  
 Sedimentation, 659  
 Seed oils, Indian, constituents of, 244, 246  
 Seeds, oil-bearing, 468  
 absorption of fumigants by, 448  
 Selenium cells, 183  
 determination of, in horticulture, 482  
 electrodeposition of, 183  
 photographic properties of, 645  
 rectifiers, 183  
 use of, in vulcanisation, 410  
 Sensitisers, chemical, 637  
 Sericin, extraction and properties of, 302  
 preparation and properties of, 313  
 Sesamin, 436  
 Sewage, analysis of, 657  
 B.O.D. test for, 657, 658  
 filtration of, 660  
 purification of, by activated-sludge process, 660  
 sedimentation of, 659  
 septicity of, 659  
 sludge, digestion of, 661  
 pathogenic organisms in, 661  
 Sewers, bacteria in, 659
- "Sexogen," 589  
 Shale, oil, distillation of, 40  
 Shark-liver oils, constituents of, 244, 245  
 hydrogenation of, 238  
 Ship bottoms, anti-fouling compositions for, 123  
 Ships, paints for, 391  
 Shoes, American Army, water penetration of, 431  
 Shrinkage temperature, 424  
 Silage, grass, 539  
 use of molasses in preparation of, 509  
 Silica bricks. *See under* Bricks  
 elimination of, from boiler water, 25  
 gel, adsorption of hydrocarbons on, 13  
 production and uses of, 186  
 production, properties, and uses of, 186  
 removal of, from water, 656  
 Silicate materials, analysis of, 264  
 Silicates, preparation of, 186  
 Silicon carbide, 277  
 in light kiln furniture, 287  
 preparation of, 186  
 determination of, 363  
 dioxide. *See* Silica  
 ingots, 185  
 tetrabromide, production of, 174  
 Silicones, 271, 303, 385  
 uses of, 363  
 Silk, azo-dyes for, 86  
 constituents of, 302  
 fibroin, mol. wt. of, 313  
 fluorescent dyes for, 101  
 Silver chloride crystals, dislocation in, 142  
 determination of, in developers, 644  
 electro-deposition of, on contact rings, 158  
 electrometallurgy of, 154  
 oxide as oxidising agent for anthraquinones, 99  
 photolytic production of, 639  
 thioacetamide, 530  
 Sintering, 278  
 Sisal fibre, extraction of, waste waters from, 666  
 Sizing, 330  
 Slags, analysis of, spectrographic, 119  
 basicity of, 111  
 control of, 111  
 Slime control in paper mills, 331  
 Slip, mechanism of, 140, 141  
 Smelters, 130  
 Smoke generators, 478  
 Smokes, control of, 208  
 insecticidal, 478  
 Snails, control of, with  $\delta$ - and  $\gamma$ -benzene hexachlorides, 442, 443  
 Soaps, 249  
 aluminium, 250  
 analysis of, 252  
 heavy metal, determination of, 253

- Sodium aluminium fluoride, 171  
 chlorate, production of, 173  
 chloride, production and specifications of, 174  
 solutions, electrolysis of, 174  
 compounds, recovery of, from alkaline pulping, 326  
 fluoride, porous, 174  
 lignate for scale removal, 26  
 oxide, determination of, in glass, 264  
 perchlorate, production of, 173  
 peroxide, pulp bleaching with, 329  
 pyrophosphate, production of, 167  
 starch glycollate as indicator in iodimetry, 561  
 sulphate, preparation and properties of, 175
- Soils, analysis of, 482  
 copper in, 455  
 fumigants for, 445, 446, 479  
 fumigation of, 446  
 manganese deficiency in, 463  
 manganese in, 456  
 mulching of, 455  
 water relations in, 454  
 wetting of, 454
- Solanine in potatoes, 533
- Solar energy, use of, for house heating, 206
- Solids, flow of gaseous suspensions of, 7
- Solvents, furan, 396  
 hydrocarbon, 396  
 nitro-compounds, 396
- Soya-bean flakes, extraction of, 236  
 oil, 378  
 flavour reversion in, 242  
 glycerides of, 243  
 heat polymerised, fractionation of, 247  
 solvent extraction of, 12, 237
- Soya beans, and their products, 538
- Sparkling-plug bodies, 370
- Sparteine, 584
- Spectra, Raman, of hydrocarbons, 224
- Spectrograph, mass, 28
- Spectrographic analysis of steel, 118
- Spectrometer, mass, for vacuum leak detection, 16
- Spectrometry, mass, of hydrocarbon mixtures, 224
- Spectroscopy, Raman, 223, 224
- Spiders, red, control of, 441, 548
- Spinning of wool, 301
- Spotted fever, Rocky Mountain, treatment of, 613
- Spraying, 24  
 from aircraft, 440  
 hydraulic, 475  
 mist, 477
- Sprays, fruit, to prolong storage-life, 530
- Spruce bark extract, fractionation of, 425  
 black, cooking of, 325
- Starch, analysis of, 496  
 cassava, 492  
 chlorination of, 496  
 constituents of, from various sources, 498, 499  
 determination of, 561  
 dust, explosion of, 494  
 enzymic synthesis of, 549  
 esters and ethers, 496  
 films, preparation of, 495  
 gels, 500  
 grains, structure and swelling of, 500  
 iodine reaction with, 499  
 maize, production of, 493  
 modified forms of, 495  
 pastes for textile finishing, 500  
 physical properties of, 499  
 potato, physical properties of, 501  
 production of, 493  
 saccharification of, 502  
 structure and constituents of, 549  
 supply of, 492  
 sweet-potato, 494  
 syrups, 502  
 wheat, 492
- Statistics in chemical industry, 32
- Steam, industrial peaks for, 209
- Steam plants for road vehicles, 203
- Stearic acid, solubility of, in acetone or hexane in presence of oleic acid, 239
- Steel, analysis of, spectrographic, 118  
 Bessemer, nitrogen removal from, 112  
 chromium plating of, 150  
 corrosion of, 121  
 by sea-water, 123  
 deoxidation of, 111, 112  
 effect of additions on properties of, 115  
 for oil industry, 223  
 gases in, 112  
 heating of, heat transfer in, 9  
 heat-treatment of, 115  
 industry, oxygen in, 285  
 ingots, solidification of, 113  
 low-temperature treatment of, 116  
 micro-radiography of, 117  
 mills, high-pressure steam plant for, 209  
 paints for protection of, 392  
 production of, 109  
 sigma phase in, 116  
 silver-plated, 154  
 stainless, 121, 122  
 electro-polishing of, 156  
 uses of, 389  
 strip, electro-tinning of, 155  
 tanks, corrosion of, 655  
 zinc flake coatings on, 389
- Sterilisation, heat, of canned foods, 534
- Steroids, 588  
 cardio-active, 590
- Sterols, degradative oxidation of, 592  
 from tall oil, 326

Stilboestrol group, 596  
     synthesis of, 596  
 Stillingia oil, 378  
 Stills, 15  
     falling-film and spinning-bowl, 17  
 Stirrers, 22  
 Stock, nutritive values of feeding-stuffs  
     for, 487  
 Stokers, automatic, 289  
     chain grate, 50  
     for brown-coal firing, 203  
 Straining plant, micro-, 653  
 Straw, cereal, for paper board, 322  
     production of, 368  
 Strawberries, freezing of, 530  
 Strength testers, 334  
 Streptidine, 575  
     synthesis of, 612  
 Streptobiosamine, 575  
*Streptococcus* in beer, 559  
 Streptocin, 614  
*Streptomyces* antibiotics, 614  
*Streptomyces aureofaciens*, aureomycin  
     from, 566  
*Streptomyces griseus*, 611  
*Streptomyces venezuelae*, 577  
 Streptomycin, 575, 610  
     assay of, 612  
     in veterinary practice, 489  
     isolation and purification of, 612  
     production of, 566, 611  
 Streptomycin B, 612  
 Streptose, constitution of, 576  
 Stress release, rate of, 263  
 Strontium carbonate, production of, 178  
 Strophanthobiase, 592  
*Strophanthus* glycosides, 591  
*Strophanthus nicholsonii*, 591  
 $\phi$ -Strychnine, 583  
 Strychnos alkaloids, 582  
 Styrene, co-polymers of, 407  
     co-polymers of drying oils with, 384  
     heat transfer in boiling water mixtures  
         of, 10  
     polymerisation of, 339  
     synthesis of, 340, 341  
 Subtenolin, 615  
 Subtilin, 614  
 Subtilin C, 578, 615  
 Sugar-beet. *See* Beetroots  
     beet-, production of, 507  
     -cane, bagasse from, 510  
         cultivation of, 511  
         insect pests and diseases of, 512  
         trash from, 511  
         wax from, 511  
     cane-, 504  
         bagasse from, 510  
         evaporators for, scale in, 505  
         plant for, 504  
         refining of, bone char process for, 506  
     crystallisation of, 510  
     decolorisation of, and of juices, 510

Sugar---continued  
     juice, beet-, processing of, 507  
     purification of, 507  
     production, 504  
     raw, micro-organisms in, 513  
     refining of, chromatography in, 508  
     syrups, dextran as stabiliser for, 513,  
         515  
 Sugar Research Foundation, 514  
 Sugars, acetylation of, 550  
     determination of, 561  
     from molasses, 509  
     methylated, chromatography of, 562  
     reducing, unfermentable, 513  
 Sulfactin, 614  
 Sulphamerazine, 488  
 Sulphamethazine, 488  
 Sulphamezathine, 488  
 Sulphates, determination of, in waste  
     liquors, 328  
 Sulphetronc, 578, 612  
 Sulphite cellulose materials, analysis of,  
     431  
     tanning with, 426  
     cooking of straw, 323  
     liquors, analysis of, 328  
         bacteria inoculated, aeration of, 664  
         disposal of, 664  
         fractionation of, 426  
         uses of, 327  
 Sulphonamides in veterinary practice, 488  
 Sulphur, colloidal, preparation of, 168  
     determination of, in coal, 210  
     dioxide as refrigerant in heat pump, 11  
     control of, in sea-water bromine  
         plants, 174  
     determination of, in beer, 560  
     latensification by, 636  
     liquid, handling of, 168  
     removal of, from flue gases, 208  
     elimination of, in blast furnaces, 106  
     in coal, 198  
     in steel, 115  
     molten, filtration of, 168  
     organic compounds, removal of, from  
         gas, 55  
     transfer of, from slag to metal, 111  
 Sulphuric acid, concentration of, 169  
     dilute, handling of, lead substitutes  
         for, 29  
     mixing phosphate rock with, 22  
     production of, 165, 168, 169  
 Sulphurous acid, production of, 168  
 Sulphydryl proteins, 306  
 Sumaloid, 506  
 Sunflower seed, 468  
 Sunflower-seed meal for feeding pigs, 539  
 Superphosphate, granulated, 459  
     production of, 460  
 Supersensitisers, 641  
 Surgical dressings, nylon films for, 363  
 Swimming baths, disinfection of, 654  
 Synergism in insecticides, 436

## T

- T.P.G., 506  
 Taint in foods, 448  
 Talc, distinction between mica, pyrophyllite, and, 440  
   grain size and particle shape in, 277  
 Tall oil, hydrogenation of, 238  
   uses of, from sulphate pulping, 326  
 Tanks, concrete, for cooling brine, 291  
   rubber lining for, 29  
 Tannery waste treatment, 432  
 Tanning, chrome, 427  
   materials from sulphite liquors, 664  
   new, 426  
   synthetic, 426  
   vegetable, 423  
 Tannins, vegetable, and collagen, 424  
   chemistry of, 425  
 Tapioca flour, supply of, 492  
 Tar, coal, distillation of, 57  
   road, adhesion of, to aggregates, 57  
   utilisation of, 57  
 Tartrazine, preparation of, 83  
 Tasting, food-testing by, 539  
 Tenite III, 369  
 Terephthalic acid, preparation of, 361  
 Terpenes, insecticidal activity of, 626  
 Terphenyls, hydrogenated, 373  
 Terpeneol as synergist for hexachlorocyclohexane, 437  
 Terylene, 361  
 Tetra-ethyl fluorophosphate as insecticide, 444  
   pyrophosphate, toxicity of, 435  
 Tetrafluorosuccinic acid, 68  
 Tetraphosphoglucosate as scale preventive, 506  
 1 (Tetrazole-5-)azo-2-naphthol, 82  
 Textile fibres, swelling of, 320  
 Textiles, crease-resisting, 319  
   drying of, 319  
 Theophylline, synthesis of, 585  
 Thermal efficiency, 60  
 Thermionic halogen vapour detector, 16  
*Thevetia nerifolia*, glycoside of, 592  
 Thevetin, 592  
 Thiamin, determination of, 537  
*Thiobacillus thio-oxidans*, 662  
 Thioindigoid dyes, 101  
 Thiophen from mineral oils, 218  
   polymerisation of, 220  
   resins from, 358  
 Thiophthen, polymerisation of, 220  
 Thorium, electrolytic production of, 155  
 Thyme oils, 625  
 Thymidine, 582  
 Ticks, blue cattle, control of, 443  
 Tin, electrometallurgy of, 155  
   electro-plating with, 155  
   -zinc alloys, plating of steel with, 156  
 Tinplate, corrosion protection of, 122  
 Tin-plating as coating under anti-corrosive paints, 390  
 Titanates, alkaline-earth, in ceramics, 278  
 Titanium compounds as dielectrics, 188  
   dioxide as opacifier in enamels, 283  
   in paper-making, 330  
   hydride, production of, 186  
   pigments, 390  
   production of, 131  
   tetrachloride, purification of, 186  
 Tobacco-seed oil, 378  
 Tocopherol, preparation of, 242  
 Toluene, analysis of, mixed with *n*-butyl alcohol and water, 397  
   production of, from petroleum, 396  
 Tomato juice, canning of, 531  
   copper in, 531  
 Tomatoes, ascorbic acid in, 473  
   effect of growth substances on, 470  
   magnesium deficiency in, 474  
 Towers, packed, pressure drop in, 6  
 Toxaphene, insecticidal effect of, 438  
 Trash for sugar-cane, 511  
 Treacle from molasses, 509  
 Trees, chemical killing of, 324  
 Trialkylbenzenes, production of, 72  
   1 : 3 : 5-Triaminobenzene, 74  
   2 : 4 : 6-Triaminotoluene, 74  
 Triarylethylenes, 597  
 Triazaindolizines as anti-foggants, 638  
 Triethanolamine in metal cleaners, 252  
 Trifluoroacetic acid, 68  
 Trifluoroethanol, 68  
 Triglyceride oils, high vacuum distillation of, 16  
   2 : 3 : 5-Triphenyltetrazolium chloride for testing damage to barley, 547  
*Trogoderma granarium*, 566  
 Trona, natural, heats of decomposition and formation of, 175  
 Tropomyosin, 422  
 Trypanocides, 490, 598  
 Trypanosomiasis, chemotherapy of, 598  
 DL-Tryptophan, 587  
 Tsetse fly, protection against, 490  
 Tubes, finned, for boiling and condensing surfaces, 10  
 Tuberculosis, treatment of, 588, 610  
 D-Tubocurarine, structure of, 584  
 Tungstates for luminescents, 188  
 Tungsten alloys, electro-deposition of, 156  
   electro-polishing of, 157  
 Turbine blades, cleaning of, 26  
 Turbines, gas, alloys for, 139  
   coal-fired, 207  
   with boilers, 203  
   gas and steam, 203  
 Turpentine, gum, purification of, 15  
   sulphate, uses of, 326  
 Tylose H.B.R., 251  
 Typhus, scrub, treatment of, 577, 613

## U

- Uraform as nitrogenous fertiliser, 359, 459  
 Uranium, electrolytic production of, 155  
   salts for luminescents, 189  
 Urea as protein-sparing material in diet, 487  
   -formaldehyde resins, 332  
 Urethanes, 385

## V

- Vacuum technology, high, 15  
 Vanadium resources, 103  
 Vanillic acid from vanillin, 75  
 Vaporisation of complex mixtures, 15  
 Varnishes, resins for, 386  
 Vegetables, blanching of, 532  
   cold-storage of, 533  
   curing of, for pickles, 533  
   dehydrated, 532  
   drying of, 535  
 Velon, production and properties of, 314  
 "Velsicol," 442  
*Verticillium* wilt on hops, 548  
 Veterinary medicines, 488  
 Vetiver oil, 621, 625  
 Vinyl isobutyl ether, polymerisation of, 348  
   chloride, 67  
     polymerisation of, 342  
       with acrylonitrile, 408  
   co-polymers, 384  
   fluoride, polymerisation of, 344  
 V-Vinylcarbazole, synthesis of, 348  
 Vinylidene fluoride, polymerisation of, 344  
 Vinylite, plasticised, creep behaviour of, 372  
 Vinylmethylnaphthalene polymers, 348  
 Viscometer, micro-, 225  
   rotation, 405  
 Viscosigraph, 500  
 Vitamins, 472  
   determination of, 537  
   in cereals, 553  
   in meat, 521  
   poultry requirements of, 484  
   retention of, in canned foods, 534  
 Vitamin-A ethers, 579  
   history and synthesis of, 578  
 Vitamin-A<sub>2</sub>, isolation of, 579  
 Vitamin-B<sub>1</sub>. *See* Aneurin  
 Vitamin-B12, 582  
 Vitamin-C. *See* Ascorbic acid  
*Vitex negundo*, essential oil from, 625  
 Vitreous systems, constitution of, 256  
 Vomisine, structure of, 583  
 Vulcanisation, 409  
   accelerators, 409

## W

- Waste waters, coal mining, 662  
   food, 662  
   oil refinery, 666  
   paper and pulp, 664  
   textile, 665  
 Water, bacteria in, 653  
   boiler, ion-exchange in treatment of, 24  
     silica removal from, 656  
   boiler-feed, oxygen removal from, 656  
   chlorination of, 653  
   coagulation and filtration of, 652  
   determination of, in fertilisers, 481  
     in leather, 430  
     spectroscopically, 397  
   distilled, production of, evaporators for, 21  
   fluoride removal from, 657  
   hard, detergent for use with, 251  
   mains, disinfection of, 654  
   manganese removal from, 657  
   pipes, corrosion of, 654  
   plumbosolvency of, 656  
   pollution, effects of, 667  
   purification, 652  
   repellency, 319  
   sea-, production of magnesite from, 179  
     treatment of, with ozone, 654  
   softening, 655  
   sorption and transport of, in soils, 454  
   trade waste, 662  
 Waxes, montan, from coal, 199  
   peat, 197  
   petroleum, properties of, 227  
   sugar-cane, 511, 515  
 Weeds, control of, 468  
   in sugar-cane, 512  
 Weevil, grain, control of, 447  
 Wetting agents, 402  
   effect of, on glass strength, 266  
 Whale meat, 522  
   oil, constituents of, 244  
 Wheat, analysis of, 528  
   flour, fortification of, with vitamins, 538  
     *See also* Flour  
   milling of, 23  
   response of, to fertilisers, 466, 467  
   sorption of fumigants by, 447  
   starch, 492  
   straw for paperboard, 323  
   "take-all" infection in, 467  
   thiamin content of, 528  
   weevily, treatment of sacks containing, 566  
 Whey, beer from, 563  
 Wind tunnels, high velocity, 5  
 Wire netting, galvanised, zinc toxicity from, covering crops, 468

Wood, carbonisation of, gas from, 49  
 for paper pulp, 322  
 grinding of, 325  
 of boats, preservative for, 391  
 preparation of, for pulping, 324  
 pulp, bleaching of, 314  
 Wool, affinity of acid dyes for, 316  
 anthraquinone dyes for, 96  
 anti-shrink treatment of, 313  
 damage to, 299  
 damaged, dyeing properties of, and  
 dye-constitution, 317  
 dipeptides from hydrolysates of, 299  
 dyeing of, 300  
 dyes for, 83  
 electron microscopy of, 296  
 fluorescent dyes for, 101  
 melanine resin treatment of, 300  
 modified, 297  
 moth-proofing of, 298  
 scouring of, 300  
   detergents for, 251  
   setting power of, effect of 2 : 4-  
   dinitrofluorobenzene on, 299  
 spinning of, 301  
 stabilisation of, 297  
 structure of, 313  
 wax, oxidation of, in storage, 300  
 Worms, army, control of, on flax, 441  
   on beet crops, 468  
 Enchytraeid, 661  
 Worsted yarns, spinning of, 302  
 Worts, analysis of, 560  
   biological sampling of, 565  
   nitrogen fractions of, 564  
   trisaccharides in, 550  
 Wrikorg-C, 506

## X

Xanthomycins, 614  
 Xenon, production of, 182  
*m*-5-Xylenol, preparation of, 73  
*o*-4-Xylidine, preparation of, 74  
*o*-4-Xylidine-*D*-ribosepyranoside, 74

## Y

Yarns, cotton, nylon, rayon, silk, photo-  
 chemical degradation of, 304  
 Yeast, brewing, 558  
   effect of freezing on, 536  
   fermentation with, 564  
   fodder, production of, 537  
   food, production of, 559  
   production and nutritive value of,  
   512, 538  
   food values of types of, 558  
   for feeding pigs, 539  
   morphology of, and classification, 556  
   phosphorus in, 557  
   purification of, 565  
   tetraploid, 556  
   washing of, 558  
 Yohimbine, 584  
 Young's modulus, determination of, 307

## Z

Zeolites as water softeners, 655  
 Zinc alkyls, use of, in hydrocarbon  
 synthesis, 219  
   corrosion protection of, 123  
   deficiency in plants, 473  
   deposition of, on oiled paper, 17  
   determination of, in beer, 561  
   dust, electrolytic production of, 155  
   flake, 389  
   hydrosulphite, pulp bleaching with,  
   329  
   oxychloride cements, paints from, 392  
   powder in paints, 389  
   silicate, manganese-activated, 189  
   sulphide, phosphorescent, grinding of,  
   189  
 Zirconium dioxide as opacifier in ena-  
 mels, 284  
   production of, 187  
   hydride, production of, 187  
   production of, 131





